IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants:	Donald R. Huffman, et al.	**Examiner:**	Tsang Foster, S.N.
Serial No.:	08/236,933	**Art Unit:**	1754
Filed:	May 2, 1994	**Docket:**	7913ZAZY
For:	NEW FORM OF CARBON		

Confirmation No.: 4115

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION OF HAROLD W. KROTO
PURSUANT TO 37 C.F.R. §1.132

Sir:

I, HAROLD W. KROTO, declare and say as follows:

1. I am currently a Professor in the Department of Chemistry and Biochemistry at the Florida State University in Tallahassee, Florida. I am also the Royal Society Research Professor in the School of Chemistry and Molecular Sciences at the University of Sussex, Brighton, United Kingdom (one of only twenty such appointments in the United Kingdom). Further, I am a visiting Professor at UCSB. Moreover, I have been awarded over one dozen honorary degrees from various universities. In 1996, I, along with Robert Curl and Richard Smalley, received the Nobel Prize in Chemistry for our discovery of fullerenes. Earlier that year, I was also awarded Knighthood for my contributions to chemistry. For the convenience of the United States Patent and Trademark Office, I have attached hereto as Exhibit 1 my curriculum vitae, which describe my credentials and demonstrate my expertise in the area of fullerenes.

2. I am intimately familiar with the literature concerning and was personally involved in the search for, C_{60} and other fullerenes. I have written several articles on the subject, as evidenced by the publications listed in Exhibit 2, including the first definitive and only complete review on the subject in Kroto, et al., in Chemical Review 1991, 91, 1213 - 1235. I therefore believe that I am among the recognized experts on the subject of fullerenes.

3. In preparing this Declaration, I have read and reviewed the subject patent application, i.e., USSN 08/236,933 in its entirety (" '933 application"), including the pending claims, which are directed to, among other things, a process for making C_{60} and C_{70} in macroscopic amounts. I have been advised that there is a companion application, USSN 486,669 (" '669 application"), on file in the United States Patent and Trademark Office. I have also been advised that, except for the claims, the disclosure in the '669 application is identical to that of the '933 application. It is my understanding that the claims in the '669 application are directed to, among other things, a process for making fullerenes in macroscopic amounts. I have also been advised of the pendency of two additional applications, namely USSN 580,246 (" '246 application") and USSN 471,890 (" '890 application"). It is my understanding that the claims of the '246 application are directed to, among other things, C_{60} and C_{70} in macroscopic amounts, while the claims of the '890 application are directed to, among other things, fullerenes in macroscopic amounts. It is my further understanding that, except for the claims, the respective disclosures are not only identical, but are also identical to the disclosure of the '933 application. I have been instructed to review the '933 application as one of ordinary skill in the art would read the application on August 30, 1990.

4. It is my opinion that the term "macroscopic amounts", as used in the claims of the '933 application, was clearly understood by one of ordinary skill in the art in 1990 at the time

of the filing of the first application in the lineage. It is my understanding that this term in the claims of the '933 application is used in its plain and ordinary meaning to connote that the process described therein produces fullerenes, including, for example, C_{60}, in amounts, which can be seen easily with the naked eye. This is consistent with the definition of "macroscopic", as defined in the McGraw Hill Dictionary of Scientific Terms, 4th ed., p.1125, 1989, where the term is defined as "large enough to be observed by the naked eye," and in Hackh's Chemical Dictionary, 4th ed., wherein it defines "macroscopic" as describing "objects visible to the naked eye."

5. "Fullerenes", in my opinion, is a term of art that is also widely understood by the scientific community; it was adopted to conveniently describe the family of caged carbon molecules, as exemplified by C_{60}. See, e.g. the section entitled "Fullerene" in the Concise Encyclopedia of Science and Technology, 3rd ed., Sybil P. Parker, ed., McGraw Hill, NY, NY, p.819 (1994), attached hereto as Exhibit 3. This section, which I prepared, defines fullerenes as an even number of carbon atoms arranged in a closed hollow cage, and specifically exemplifies fullerene-60 or C_{60}, as a species of fullerenes. However, there are other species of fullerenes, and many of those can and have been prepared by the process described in the '933 application in macroscopic amounts.

6. This Declaration supplements (and is not intended to replace) the previous Declarations, which were executed on July 27, 1995 and June 9, 1995, and November 16, 1999, the contents of all of which are incorporated herein by reference.

7. I have been requested by applicants' attorney to supplement the Declarations identified in Paragraph 6. In particular, I have been asked to repeat the experiments as described in the '933 application and to describe in more detail, relative to the aforementioned

Declarations, the protocols used and the evidence obtained therefrom that show that fullerenes, for example, C_{60} and C_{70}, are produced, in accordance with the teachings in the '933 application, in macroscopic amounts.

8. In particular, I have been requested by applicants' attorney to prepare the fullerenes in accordance with the procedure described in the '933 application at two different pressures, viz., at 100 torr and 2 atm pressure.

9. I have repeated the experiments described in the '933 application several times prior to the most recent request by applicants' attorney, and as indicated in my earlier testimony, macroscopic amounts of C_{60} and C_{70} and other fullerenes have been produced in accordance with the procedure described therein. This testimony in this Declaration confirms my earlier testimony provided in the aforementioned Declarations.

10. Initially, it is to be noted, that the bell jar apparatus, described in the '933 application, is no longer being utilized today; thus the apparatus for preparing fullerenes had to be set up, in accordance with the teachings in the '933 application, before experiments in this endeavor were commenced.

11. Moreover, I no longer am conducting research in the fullerene area. In particular, my laboratory is no longer equipped to produce fullerenes.

12. I so advised applicants' counsel, and it was agreed that I would coordinate the performance of the requested experiments by colleagues of mine.

13. I instructed Mauricio Terrones in Mexico ("Dr. Terrones") to prepare the soot in accordance with the procedure described in the '933 application and especially Example 1 in the '933 application.

14. Dr. Terrones set up the bell jar apparatus as described in the '933 application for the vaporization of the graphite rods. It is my understanding that this bell jar apparatus used by Dr. Terrones was identical in every way to the bell jar apparatus described in the '933 application. However, it had one constraint. The vaporization to form the soot could only be conducted for at most about 2 minutes per run at 100 torr. Moreover, to conduct the vaporization at the higher pressure, i.e., 2 atm, the bell jar apparatus was modified by replacing the glass cover with an aluminum cover, which was adopted with stoppers and bolts/nuts to keep the aluminum cover in place (hereinafter this modified bell jar apparatus will be referred to as an "aluminum reactor"). This aluminum reactor was equivalent to the bell jar apparatus described in the '933 application. However, this aluminum reactor also had the same constraints, as the bell jar apparatus described above, except that vaporization conducted at 2 atm was performed in two to three segments, each no longer than about 25 seconds at a time.

15. Dr. Terrones conducted the experiments to produce the soot in accordance with the procedure described in the '933 application, and especially Examples 1 and 2, thereof, at two different pressures, one at 2 atm and the other at 100 torr, using a current of about 100 amps. Dr. Terrones vaporized graphite rods of ¼ inch in diameter, with a one-centimeter length of the tip of each rod being reduced in diameter to about 5 millimeters, at 100 torr and 2 atm, following the procedure described in the '933 application.

16. In accordance with the procedure described in the '933 application, Dr. Terrones collected 1 gram of soot at the lower pressure by performing several runs at the lower pressure; about 100 mg. of soot, on average, was obtained from each run.

17. In an effort to meet the time schedule imposed by the United States Patent and Trademark Office described above, Dr. Terrones did not attempt to collect one gram of soot at

the higher pressure, but instead chose to separate the fullerenes that were produced from a run conducted at 2 atm.

18. To economize the time, and to meet the deadline imposed by the United States Patent Office, I did not have Dr. Terrones separate the fullerenes from the soot. I decided to have the soot produced by Dr. Terrones at the lower pressure forwarded to my colleague, Professor Adam Darwish, at Sussex University, for the separation of fullerenes from the soot. In this way, there would be a minimum loss of time, as Dr. Darwish would be isolating fullerenes from the soot, while Dr. Terrones was effecting the vaporization of graphite at the higher pressure.

19. Dr. Darwish utilized standard chemical techniques to separate the C_{60}, C_{70} and the other fullerenes from the soot, described in the '933 application and/or known and routine to one of ordinary skill in the art in September 1990. Specifically, Dr. Darwish used soxhlet extraction and preparative HPLC, which are techniques which were known and routine to one of ordinary skill in the art in September 1990.

20. From the 1g sample of soot produced at 100 torr, Dr. Darwish collected 65 mg of C_{60}, crystals, 15 mg of C_{70} and 1-5 mg of the higher fullerenes (i.e., fullerenes other than C_{60} and C_{70}). Mass spectra data confirmed the products produced. The C_{60}, C_{70}, and the total amount of the higher fullerenes obtained from the soot produced from the vaporization of graphite at 100 torr, in accordance with the procedure described in the '933 application were produced in macroscopic amounts.

21. Attached hereto as Exhibit 4 is evidence of the C_{60} produced at the lower pressure from the vaporization of graphite in the bell jar apparatus at the lower pressure, produced in accordance with the procedure described in the '933 application. Exhibit 4(a) is the mass

spectrum of the C_{60}, which verifies that the product is C_{60}. Moreover, the clean spectra as well as the HPLC tracing in Exhibit 4(b) show that the C_{60} produced is relatively pure. Exhibit 4(c) is a photograph of a sample of C_{60} dissolved in toluene, and Exhibit 4(d) is a photograph of the crystals of C_{60} produced at the lower pressure after evaporation of the toluene. As shown in Exhibit 4(d), the C_{60} produced at the lower pressure was present in macroscopic amounts. In fact, 65 mg of the C_{60} product, which was isolated from the soot produced from the vaporization of graphite at 100 torr, can easily be seen with the naked eye.

22. Attached hereto as Exhibit 5 is evidence of the C_{70} isolated from the soot at the lower pressure from the vaporization of graphite, produced in accordance with the procedure described in the '933 application. Exhibit 5(a) is the mass spectrum of the C_{70} isolated from the soot produced from the graphite at 100 torr, confirming that the product produced is C_{70}. Moreover, the mass spectrum as well as the HPLC tracing in Exhibit 5(b) show that the C_{70} produced is relatively pure. Exhibit 5(c) is a photograph of a sample of C_{70} dissolved in toluene and Exhibit 5(d) is a photograph of a sample of the crystals of C_{70} produced at the lower pressure after evaporation of toluene. As shown by Exhibit 5(d), the C_{70} produced at the lower pressure was present in macroscopic amounts. In fact, 15 mg of product, which is the amount of C_{70} produced from the soot produced from the vaporization of graphite at 100 torr, can easily be seen with the naked eye.

23. The amount of the higher fullerenes (i.e. fullerenes other than C_{60} and C_{70}) collected in total from the soot prepared from the vaporization of graphite at the lower pressure, in accordance with the procedure described in the '933 application, was also produced in macroscopic amounts; 7 mg of the higher fullerenes, which were collected from the soot produced from the vaporization of graphite at 100 torr, also can be seen with the naked eye.

From the data, the following fullerenes were also isolated from the vaporization at the lower pressure, the identities of which were confirmed by mass spectra: $C_{70}O$, C_{76}, C_{78}, C_{84}, C_{86}, and C_{90}.

24. Reference is made to Exhibit 6. The upper portion depicts photographs of samples of each of the fullerenes discussed in the previous paragraph dissolved in toluene together with photographs of the crystals formed from evaporation of exactly the half volume of the toluene solution obtained, except for C_{86}, where all the toluene solution was evaporated to dryness, while the lower photographs show crystals of each of the fullerenes discussed in Paragraph 24 obtained from the evaporation of toluene. As evidenced by the photographs of the crystals of each of these fullerene products identified in the previous paragraphs, these crystals were seen with the naked eye.

25. Dr. Darwish also separated C_{60}, C_{70} and higher fullerenes from the 100-mg. sample produced by Professor Terrones when the vaporization was conducted at the higher pressure of 2 atm. using a current of 100 amps, following the procedure described in the '933 application. The discussion in paragraphs 27-31 relates to the results of this experiment.

26. From the 100 mg sample produced at 2 atm and 100 amps, Dr. Darwish obtained 9 mg or 9% yield of fullerenes. He isolated 5.0 mg of C_{60} crystals, 1.5 mg of C_{70} crystals and 1.0 mg of higher fullerenes from the soot.

27. The mass spectrum of the C_{60} sample produced at 2 atm is depicted in Exhibit 7, confirming that C_{60} was produced and was relatively pure. A sample was dissolved in toluene, and when the toluene was evaporated, C_{60} crystals were collected. Exhibit 7 also includes a photograph of the C_{60} dissolved in the toluene solution and a photograph of the C_{60} crystals obtained from the evaporation of toluene. Thus, as shown by the photograph of the C_{60} crystals

in Exhibit 7, C_{60} was isolated in macroscopic amounts from the 100 mg sample of soot produced by Dr. Terrones from the vaporization of graphite at the higher pressure, prepared in accordance with the procedure described in the '933 application.

28. The mass spectrum of the C_{70} sample produced at 2 atm is depicted in Exhibit 8, confirming that the C_{70} that was produced was relatively pure. A sample of the C_{70} was dissolved in toluene and when the toluene was evaporated, C_{70} crystals were produced. Figure 8 also includes a photograph of a sample of C_{70} solution in toluene and a photograph of the C_{70} crystals produced after evaporation of the toluene. Thus, as shown by the photograph in Exhibit 8, the C_{70} crystals can be seen with the naked eye. Thus, C_{70} was isolated in macroscopic amounts from the 100 mg sample of soot produced from the vaporization of graphite at 2 atm, prepared in accordance with the procedure described in the '933 application.

29. Besides C_{60} and C_{70}, higher fullerenes ("HFs") were produced. In fact, the mass spectrum provides evidence that higher fullerenes up to C_{104} were produced at the higher pressure. A copy of the mass spectrum is attached hereto as Exhibit 9. A sample of the higher fullerenes, obtained from the 100 mg sample of soot that was obtained from the vaporization of soot at 2 atm, was dissolved in toluene and when the toluene was evaporated, crystals of the higher fullerenes were produced. Exhibit 9 also includes a photograph of a sample of the higher fullerenes dissolved in toluene and a photograph of the solid crystals that were formed after evaporation of the solvent. The photograph shows crystals of higher fullerenes that can be seen with the naked eye. Thus, macroscopic amounts of the higher fullerenes were obtained from the vaporization of graphite at 2 atm, prepared in accordance with the procedure described in the '933 application.

30. Exhibit 10 depicts the photographs of C_{60}, C_{70} and the higher fullerenes in solution in toluene that were isolated from the 100 mg sample of soot produced from the vaporization of graphite at 2 atm pressure, prepared in accordance with the procedure described in the '933 application and the photographs of crystals of C_{60}, C_{70} and the higher fullerenes that were obtained after evaporation of the toluene. Inasmuch as the crystals of C_{60}, C_{70}, and the higher fullerenes were visible, as evidenced by the photographs in Exhibit 10, the C_{60}, C_{70} and higher fullerenes were produced in macroscopic amounts from the vaporization of graphite at the higher pressure, prepared in accordance with the procedure described in the '933 application.

31. It is observed that the bell jar apparatus and the aluminum reactor were both limited by the constraint that only permitted the vaporization to be conducted for a limited time before the vaporization had to be stopped. Nevertheless, even with this constraint, in the present circumstances, the process described in the '933 application produced macroscopic amounts of C_{60}, C_{70} and higher fullerenes when the process was conducted at both the lower pressures of 100 torr and at the higher pressure of 2 atm.

32. As shown by the data produced by the experiments conducted in accordance with the process described in the '933 application, as described herein, C_{60} and C_{70} and other fullerenes produced were obtained in amounts that could be seen with the naked eye. The C_{60}, C_{70} and the higher fullerenes were produced in macroscopic amounts. See Exhibits 4-10.

33. Thus, by following the procedure described in the '933 application, the evidence provided herein shows that the process described in the application produces several species of fullerenes, including C_{60}, C_{70} and higher fullerenes in macroscopic amounts, both at the lower pressure, i.e., 100 torr, and at the higher pressure, 2 atm.

34. Moreover, the results described hereinabove show that a high yield of fullerenes is recovered from the soot prepared in accordance with the procedure described in the '933 application; approximately 10% of the soot was comprised of fullerenes. This is still among the highest yield of fullerenes obtained from soot to date. From the mass spectrum, it is evident that fullerenes other than those characterized herein were present in the soot, macroscopic amounts of these other fullerenes may be isolated if additional runs were performed.

35. The soot was prepared by Dr. Terrones merely following the procedure described in the '933 application, especially Examples 1 and 2; there was no undue amount of experimentation in the preparation thereof. Further, the separation of macroscopic amounts of fullerenes including C_{60} and C_{70} from the soot was routine to one of ordinary skill in the art on August 30, 1990. Thus, the process described in the '933 application is sufficiently detailed for the skilled artisan on August 30, 1990 to prepare macroscopic amounts of C_{60} and C_{70}, without undue experimentation.

36. The realization by Huffman and Kratschmer of macroscopic quantities of fullerene, e.g., C_{60} and C_{70} and the isolation and characterization of same, e.g., C_{60} and C_{70} by the methods described in the '933 application are recognized by the knowledgeable scientific community as a long awaited and much needed breakthrough; it was surprising that relatively high yields of fullerenes, such as C_{60}, could be achieved by these methods. The difficulties that existed in the quest for C_{60} are well elaborated in the article entitled "Fullerenes" by Robert F. Curl and Richard E. Smalley, printed in Scientific American, Oct. 1991, pp. 54-62 attached hereto as Exhibit 11.

37. Although the discovery described in the Huffman and Kratschmer application may seem simplistic to the uninformed, especially in hindsight, their discovery was quite

remarkable. The Kratschmer and Huffman method described in the '933 application is all the more remarkable for the fact that so simple a procedure so readily produces large amounts of fullerenes. This is readily appreciated if one considers the historical perspective. Even since the detection of C_{60} by the collaborative efforts of the Smalley and Kroto groups in 1985, as described in the article in Nature, 1985, 318, 162-163, attached hereto as Exhibit 12, experts, such as Drs. Smalley and myself, both together and separately worked to prepare fullerenes on a larger scale. For five long years, many attempts were tried, but each was unsuccessful. Finally, to my expert knowledge, one group, Huffman and Kratschmer, was the first to find and publish a methodology capable of producing and isolating fullerenes, such as C_{60}, in macroscopic amounts. This methodology is described in the '933 application and satisfied a long felt need in this area.

38. The scientific community has unanimously and unequivocally acknowledged and recognized that Kratschmer and Huffman were the first to have developed a process for preparing and isolating fullerenes, e.g., C_{60}, in macroscopic amounts, and were the first to isolate the fullerenes, e.g., C_{60}, in macroscopic amounts and in consequence thereof has presented them with several awards. Even the press release by the Royal Swedish Academy of Sciences regarding the Nobel Prize in Chemistry in 1996, attached hereto as Exhibit 13, recognized the contribution of Huffman and Kratschmer by acknowledging that these two scientists for the first time produced "isolable quantities of C_{60}". (See Page 2 of Exhibit 13). As stated in the press release:

> [t]hey obtained a mixture of C_{60} and C_{70} the structures of which could be determined...The way was thus open for studying the chemical properties of C_{60} and other carbon clusters such as C_{70}, C_{76}, C_{78} and C_{84}...An entirely new branch of chemistry developed with consequences in such diverse areas as

astrochemistry, superconductivity and materials chemistry/physics.

39. Thus, in my opinion, the '933 application describes a process for preparing fullerenes, including C_{60}, in macroscopic amounts and the process described therein provides sufficient detail for an ordinary skilled artisan in August 1990 to make the same in the absence of undue amount of experimentation.

40. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: 27 Aug 07

Harold W. Kroto, Ph.D.

CURRICULUM VITAE

Part A

Professor Sir Harold Kroto FRS

Born 1939 Wisbech Cambridgeshire, educated Bolton School. BSc (First class honours degree Chemistry, 1961) and a PhD (Molecular Spectroscopy, 1964) University of Sheffield. Postdoctoral work at the National Research Council (Ottawa, Canada 1964-66) and Bell Telephone Laboratories (Murray Hill, NJ USA 1966-67); Tutorial Fellow 1967, lecturer 1968, Reader 1977University of Sussex (Brighton) in 1967. He became a professor in 1985 and a Royal Society Research Professor in 1991. In 1996 he was knighted for his contributions to chemistry and later that year, together with Robert Curl and Richard Smalley (of Rice University, Houston, Texas), received the Nobel Prize for Chemistry for the discovery of C_{60} Buckminsterfullerene a new form of carbon.

Research fields cover several major topics:

1) (1961-1970) Electronic spectroscopy of free radicals and unstable intermediates in the gas phase, ii) Raman spectroscopy of intermolecular interactions in the liquid phase and iii) Theoretical studies of electronic properties ground and excited states of small molecules and free radicals.
2) (1970-1980) Research focused on the creation of new molecules with multiple bonds between carbon and elements, mainly of the second and third row of the Periodic Table (S, Se and P), which were reluctant to form such a link. These studies showed that many of these previously assumed impossible species could be produced, studied by spectroscopy and used as valuable synthons leading to a wide class of new phosphorus containing compounds. In particular the spectroscopic studies of molecules with carbon-phosphorus multiple bonds (C=P and C≡P) were the pioneering studies that initiated the now prolific field of Phosphaalkene/alkyne Chemistry.
3) (1975-1980) Laboratory and radioastronomy studies on long linear carbon chain molecules (the cyanopolyynes) led to the surprising discovery (by radioastronomy) that they existed in interstellar space and also in stars. Since these first observations the carbon chains have become a major area of modern research by molecular spectroscopists and astronomers interested in the chemistry of space.
4) (1985-1990) The revelation (1975-1980) that long chain molecules existed in space could not be explained by the then accepted ideas on interstellar chemistry and it was during attempts to rationalise their abundance that C_{60} Buckminsterfullerene was discovered. Laboratory experiments at Rice University, which simulated the chemical reactions in the atmospheres of red giant carbon stars, serendipitously revealed the fact that the C_{60} molecule could self-assemble. This ability to self-assemble has completely changed our perspective on the nanoscale behaviour of graphite in particular and sheet materials in general. The molecule was subsequently isolated independently at Sussex and structurally characterised.
5) (1990-) Present research focuses on Fullerene chemistry and the nanoscale structure of new materials, in particular nanotubes. This has led to a wide range of new nanostructured materials the first insulated nanowires and new perspectives on the mechanism of nanotube formation.

Key collaborations: With D R M Walton (Sussex), T Oka, L Avery, N Broten and J MacLeod (NRC Ottawa) on carbon chain molecules in the laboratory and space; J F Nixon on phosphaalkene/alkyne chemistry (at Sussex); with J P Hare, P R Birkett, A Darwish, M Terrones, W K Hsu, N Grobert, Y Q Zhu, R Taylor and D R M Walton on Fullerene chemistry and nanostructures (at Sussex); with R F Curl, J R Heath, S C O'Brien, Y Liu and R E Smalley (at Rice University Texas) on the discovery of Buckminsterfullerene.

Education: Chairman of the board of the Vega Science Trust which is produces science programmes for network television. 75 have been made and so far 55 have been broadcast on the BBC Learning Zone educational slot. Member of National Advisory Committee on Cultural and Creative Education.

Scientific Awards etc: Tilden Lectureship of the RSC (1981); International Prize for New Materials by the American Physical Society (shared 1992 with Robert Curl and Richard Smalley); Italgas Prize for Innovation in Chemistry (1992); Royal Society of Chemistry Longstaff Medal (1993); Hewlett Packard Europhysics Prize (shared with Wolfgang Kraetschmer, Don Huffman and Richard Smalley 1994);

Nobel Prize for Chemistry in 1996 (shared with Robert Curl and Richard Smalley); American Carbon Society Medal for Achievement in Carbon Science (shared with Robert Curl and Richard Smalley1997); Blackett Lecturship 1999 (Royal Society); Faraday Award and Lecture 2001 (Royal Society). Dalton Medal 1998 (Manchester Lit and Phil), Erasmus Medal of Academia Europaea, Ioannes Marcus Marci Medal 2000 (Prague) for contributions to molecular spectroscopy.

Fellowships etc: Fellow of the Royal Society (1990), Fellow of the Royal Society of Chemistry; President of the Royal Society of Chemistry (2002-2004), Mexican Academy of Science; Member Academia Europaea (1993); Hon. Foreign Member Korean Academy of Science and Technology (KAST) (1997); Hon. Fellow of the Royal Microscopical Society (1998); Hon. Fellow of the Royal Society of Edinburgh (1998); Hon Fellow of the RSC (2000).

Honorary degrees: Université Libre (Bruxelles), Stockholm (Sweden), Limburg (Belgium), Sheffield, Kingston, Sussex, Helsinki (Finland), Nottingham, Yokohama City (Japan), Sheffield-Hallam, Aberdeen, Leicester, Aveiro (Portugal), Bielefeld Germany), Hull, Manchester Metropolitan, Exeter, Hong Kong City (China), Gustavus Adolphus College (Minnesota, USA), University College London, Patras (Greece), Halifax (NovaScotia, Canada), Strathclyde; Hon Fellowship: Bolton Institute.

Graphic design work has resulted in numerous posters, letterheads, logos, book/journal covers, medal design etc. Awards: Sunday Times Book Jacket Design competition (1964) and more recently the Moet Hennessy/Louis Vuitton Science pour l'Art Prize (1994). Citation in the international design annual "Modern Publicity" (1979) for the cover of "Chemistry at Sussex"

TV/Internet Science Programmes: Prix Leonardo Bronze Medal (2001); Chemical Industries Association (Presidents prize short list1998 and 1999)

Harry Kroto's Curriculum Vitae

Part B - Harry's main research intrests and research highlights

Main research areas:

I Spectroscopy of Unstable Species and Reaction Intermediates (Infrared, Photoelectron, Microwave and Mass Spectrometry)
II Astrophysics (Interstellar Molecules and Circumstellar Dust)
III Cluster Science (Carbon and Metal Clusters, Microparticles, Nanofibres)
IV Fullerene Chemistry, Nanoscience and Nanotechnology

Research Highlights (Ref Nos - Key Refs List)

a) First detection of $^1\Delta$ state of a polyatomic free radical (NCN by flash photolysis) [3,4]
b) Theoretical studies of ground and electronically excited sates of small molecules [5,6]
c) Detection of liquid phase intermolecular interactions using Raman Spectroscopy [7-10]
d) Breakthrough in the detection of new unstable species (thioaldehydes, thiocarbonyls thioborines) using combination of microwave and photoelectron spectroscopy techniques [12,15,18-22,31,80]
e) Synthesis in 1976 of the first phoaphaalkenes (compounds containing the free carbon phosphorus double bond) in particular CH2=PH (with N P C Simmons and J F Nixon, Sussex), [28, 80]
f) Monograph "Molecular Rotation Spectra" [23]
g) Synthesis in 1976 of the first analogues of HCP, the phosphaalkynes which contain the carbon phoshorus triple bond - in particular CH3CP (with N P C Simmons and J F Nixon, Sussex), [29,80]
h) The discovery (1976-8) of the cyanopolyynes, HCnN (n=5,7,9), in interstellar space (with D R M Walton A J Alexander and C Kirby (Sussex) and T Oka, L W Avery, N W Broten and J M MacLeod (NRC Ottawa)), Ref 4-6, based on microwave measurements made at Sussex, [27,30,35,80]
i) The discovery of C60: Buckminsterfullerene in 1985 (with J R Heath, S C O'Brien, R F Curl and R E Smalley), [100,112,139,239]
j) The detection of endohedral metallofullerene complexes (with J R Heath, S C O'Brien, Q Zhang, Y Liu, R F Curl, F K Tittel and R E Smalley), [101,139]

k) The prediction that C60 should be produced in combustion processes and might indicate how soot is formed (with Q L Zhang, S C O'Brien, J R Heath, Y Liu, R F Curl and R E Smalley) [103,139]

l) The explanation of why C70 is the second stable fullerene (after C60) and the discovery of the Pentagon Isolation Rule as a criterion for fullerene stability in general [107,112,139,239]

m) The prediction of the tetrahedral structure of C28 and the possible stability of "tetravalent" derivatives such as C28H4 [107,112,139,239]

n) The prediction that giant fullerenes have quasi-icosahedral shapes and the detailed structure of concentric shell graphite microparticles (with K G McKay), [111,112,139,239]

o) The mass spectrometric identification and solvent extraction (with J P Hare and A Abdul-Sada) of C60 from arc processed carbon in 1990 - independently from and simultaneously with the Heidelberg/Tucson group; Refs [121,239]

p) The chromatographic separation/purification of C60 and C70 and 13C NMR measurements which provided unequivocal proof that these species had fullerene cage structures (with J P Hare and R Taylor, Sussex), Refs [121,139,239]

q) Crystal structure of C60 [135,138]

r) Main Fullerene chemistry breakthroughs: C60(ferrocene)2 [162], characterisation of C60Hal6 [174,149], C60(P4)2 [187], [192]

s) Nanoscience and Nanotechnology advances: Condensed phase nanotubes [205], nanoscale BN structures [224], partly aligned-nanotube bundles [233], nanotube formation mechanisms [161,238], silicon oxide nanostructures [247], Si surface-deposited fullererene studies [251], insulated carbon nanotube conductors [297]

NB General review refs underlined

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General Information   Publication List

Publications: 1963 To 2002

As the publication list is large it has been broken down chronologically into four parts

The first part 1963 - 1984, is contained on this page, if however you are looking for information on other years please click one of the following links:

Years: 1963 - 1984 1985 - 1993 1994 - 2000 2001 - 2002

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Publications: 1985 - 1993

Years: 1963 - 1984 1985 - 1993 1994 - 2000 2001 - 2002

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Chem. Rev. 1991, 91, 1213–1235

C_{60}: Buckminsterfullerene

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Received May 2, 1991 (Revised Manuscript Received July 26, 199:

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Harry Kroto (left) was educated at Sheffield University and after periods at the National Research Council, Canada (1964–1966), and Bell Telephone Laboratories (1966–1967) went to the University of Sussex where he is now Professor of Chemistry. His research into the production and spectroscopic characterization of new species such as the phospahaalkenes, phospahaalkynes, thiocarbonyls, and polyynes led, via radioastronomy studies of interstellar molecules, to carbon cluster beam experiments aimed at understanding stellar chemistry. Wahab Allaf (right) who was educated at Aleppo University (Syria) and Sussex University is carrying out research on carbon clusters and laser chemistry. Simon Balm (center) who is studying cluster beam reactions and astrophysical chemistry was educated at Durham University and Sussex University.

I. Introduction

In 1967 Palmer and Shelef wrote the definitive review of the early work on carbon clusters in their article on the composition of carbon vapor.[1] Major advances have however been made in the interim period, and the overall situation has been updated by Weltner and Van Zee[2] who have given a very complete picture of the state of this fascinating field. Although Weltner and Van Zee's review is comprehensive (up to Nov 1, 1988), covering all aspects of carbon cluster properties, recent advances in the story of C_{60} buckminsterfullerene (Figure 1) indicate that a specialized review is necessary and timely. The existence of the fullerenes as a family has now been established and it is useful to use a convenient nomenclature such as fullerene-60 or fullerene-70 which can apply to the whole family. There are of course numerous possible C_{60} and C_{70} cage isomers, however here we shall, in general, mean the most geodesically stable cages for which there is now no doubt in the case of the 60 and 70 atom species—they are (I_h)fullerene-60 and (D_{5h})fullerene-70 where standard symmetry labels have been added as prefixes. Since the existence of fullerene-60 and its spontaneous creation have ramifications in numerous areas from the properties of carbonaceous solids and microparticles through combustion, thermolysis, and synthetic organic chemistry to the nature of the carbonaceous constituents of space, these implications are also surveyed.

During a series of experiments in 1985 which probed the nature and chemical reactivity of the species produced during the nucleation of a carbon plasma the C_{60} species was discovered to be stable by Kroto, Heath, O'Brien, Curl, and Smalley.[3] It was proposed that this stability was due to geodesic and electronic properties inherent in the truncated icosahedral cage structure shown in Figure 1 and the molecule was named buckminsterfullerene. This novel proposal did not receive instant universal acceptance since it appeared to have been based on highly circumstantial evidence. Indeed it is now clear that there was a significant degree of scepticism in the minds of some with regard to the validity of the proposal, perhaps because the evidence was dispersed among many disparate scientific observations, much like the way that C_{60} itself may—we now realize—be involved in many processes involving carbon in the environment and space. However, systems giving rise to C_{60} were subjected to many detailed investigations subsequent to the discovery paper,[3] and some important points evolved which are worthy of highlighting:

(i) A wealth of convincing experimental evidence was amassed that showed that C_{60} possessed unique physicochemical stability—a conclusion totally independent of the cage structure proposal.

(ii) The fullerene cage proposal was the simplest and most elegant explanation of the unique behavior and no serious alternative explanation was ever presented.

KROTO EXHIBIT 2

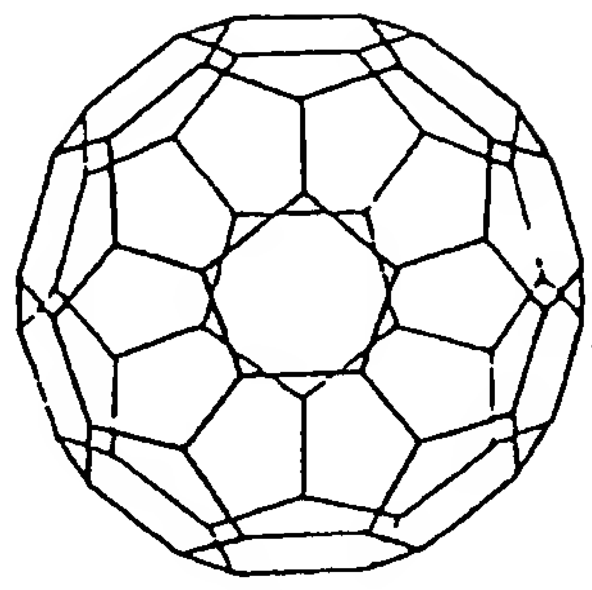

Figure 1. C_{60} buckminsterfullerene.[3]

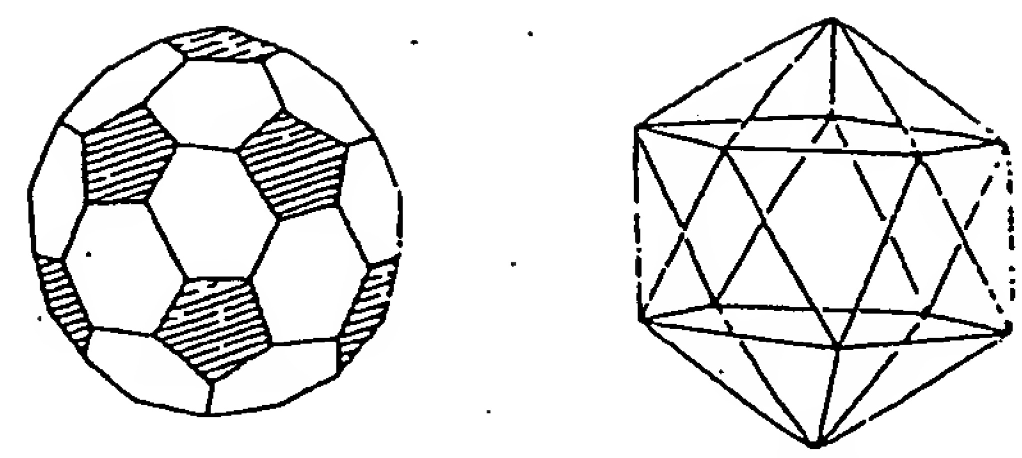

Figure 2. Diagram of C_{60} next to an icosahedron published in the book *Aromaticity* by Yoshida and Osawa.[14] These authors discuss (in Japanese) the "superaromaticity" which might accompany electron delocalization over a three dimensional truncated icosahedral pure carbon molecule.

(iii) The proposal was consistent with many earlier observations on bulk carbon and clarified some previously unexplained phenomena in carbon chemistry.

The fullerene structural proposal has recently been confirmed by complementary observations from two groups. Krätschmer, Lamb, Fostiropoulos, and Huffman,[4] in following up their earlier IR investigation (in 1989)[5] which suggested that C_{60} might be present in arc-processed graphite, extracted a soluble material which formed crystals. The X-ray analysis showed the material to consist of 10-Å diameter spheroidal molecules and supplementary mass spectrometric and infrared data provided the first unequivocal evidence for C_{60} (and C_{70}). In a parallel, independent investigation which probed this same original key observation,[5] Taylor, Hare, Abdul-Sada, and Kroto[6] found that similarly arc-processed graphite gave rise to a 720 mass peak, commensurate with the presence of fullerene-60, and that this material was soluble and could be extracted directly. The extracted C_{60} compound yielded a single ^{13}C NMR line which proved that all 60 carbon atoms are equivalent as expected for the truncated icosahedral buckminsterfullerene structure. Taylor et al. also showed that C_{60} and C_{70} can be separated chromatographically and that the latter has the D_{5h} prolate, ellipsoidal structure first suggested by Heath et al.[6] These results provide further support for the conjecture that a whole family of fullerenes exists.[7,8]

Since these revelations, which are discussed further in section IX, the fullerene field has exploded and numerous groups are probing various facets of physicochemical properties of the fullerenes. Indeed a new field of carbon chemistry has been born, and the first faltering steps of the promising infant are described in section X. Thus this review is particularly timely as it is written at the precise moment when the final sentence in the last paragraph of the *first* chapter in the story of the fullerenes has been completed. The opening paragraphs in the next chapter are just being written and they herald a new era in which the flat world of polycyclic aromatic chemistry has been replaced by a postbuckmisterfullerene one in which round structures are favored under certain surprisingly common circumstances.[10] This article reviews the buckminsterfullerene story from the time when it was just a twinkle in the eyes of a few imaginative theoreticians, through the experiments which revealed that it actually formed spontaneously and exhibited stability to the most recent revelations that it could be isolated and did indeed possess the round hollow cage structure as proposed. As many contributions to the story as could be traced by Dec 1990 are included.

II. Summary of Relevant Carbon Studies Prior to the Discovery of C_{60} Stability

At least part of the reason for the degree of interest engendered by the buckminsterfullerene proposal revolves around its high degree of symmetry. Mankind has always been fascinated by symmetric objects, indeed stone artifacts with the form of the Platonic solids, dating back to neolithic times, have been found in Scotland,[11] indicating that human beings have long had a spiritual affinity with abstract symmetry and an aesthetic fascination for symmetric objects. The truncated icosahedron is one of the Archimedian semiregular *solids*; however in *hollow* form an early example appears in the book *De Divina Proportione* by Fra Lucia Pacioli. A reproduction of this drawing by Leonardo Da Vinci entitled "VCOSEDRON ABSCISVS VACVVS" is to be found in the book *The Unknown Leonardo*,[12] which is rather more accessible than the original!

The C_{60} molecule itself was first suggested in a most imaginative and prescient paper by Osawa in 1970[13] and discussed further in a chapter on "Superaromaticity" in a book by Yoshida and Osawa[14] in 1971; the original diagram is depicted in Figure 2. An equally imaginative article, which actually predates this work, was written in 1966 by Jones in which he conjectured on the possibility of making large hollow carbon cages.[15,16] The next paper was that of Bochvar and Gal'pern in 1973 who also published a Hückel calculation on C_{60}.[17,18] In 1980 Davidson published a paper which used graph theory to deduce an algebraic solution of the Hückel calculation for fullerene-60.[19] Davidson's orbital energy level diagram, depicted in Figure 3, was determined by using a calculator, and this paper contains an unusually prescient paragraph in the light of recent observations (particularly those in section VII): "Should such structures or higher homologs ever be rationally synthesized or obtained by pyrolytic routes from carbon polymers, they would be the first manifestations of authentic, discrete three-dimensional aromaticity." Haymet's study[20] on this molecule coincided very closely with its discovery in 1985.[3]

On the experimental front there were many very important early papers on carbon clusters and these have already been reviewed.[1,2] Perhaps the most interesting early carbon cluster papers (and the ones which in fact actually stimulated the discovery experiments) were

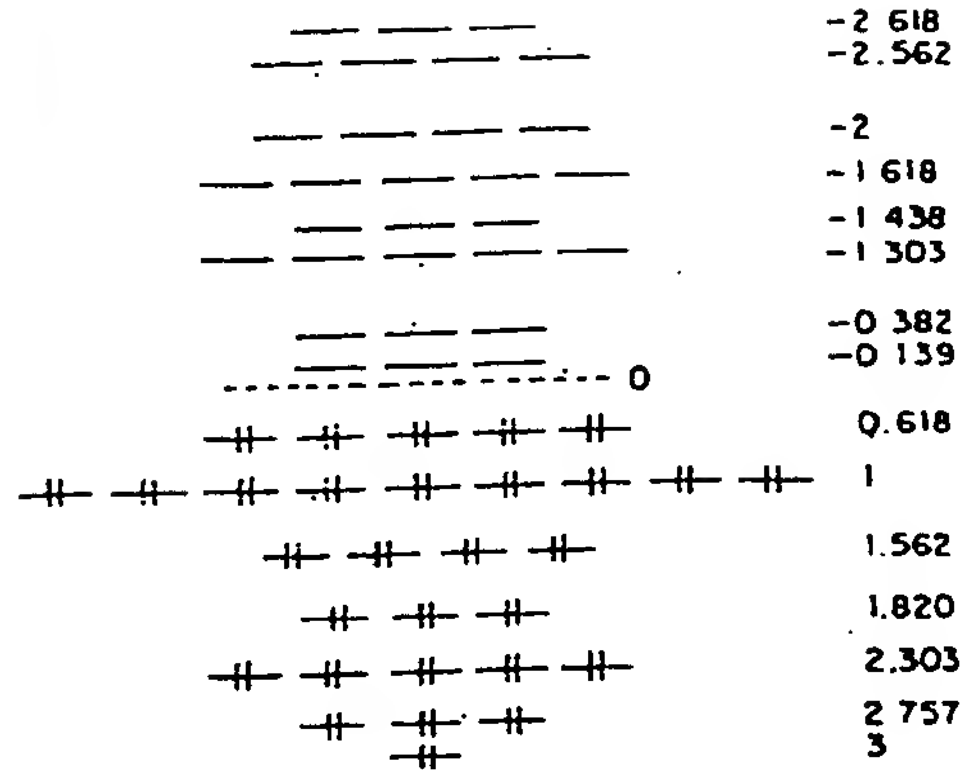

Figure 3. The Hückel molecular orbital calculation for buckminsterfullerene was carried out by Bochvar and Gal'pern[17,18] (1973) and Davidson[19] (1980), prior to, and by Haymet[20] (1985) coincidentally with, its discovery. The orbital energy level diagram (units of β) depicted here is that published by Davidson[19] who determined it using graph theory to obtain simplified algebraic relations which were evaluated with a calculator (reprinted from ref 19; copyright 1981 Springer-Verlag Publishers).

those published by Hintenberger and co-workers in 1959–63[21-24] in which it was shown that species with up to 33 carbon atoms could form in a carbon arc. The next important advance was made by Rohlfing, Cox, and Kaldor[25] in 1984 who found that much larger carbon clusters (C_n with $n = 30$–190) could be produced by vaporization of graphite (Figure 4). Rohlfing et al. used the supersonic nozzle, laser vaporization technique developed by Smalley and co-workers at Rice University[26] in 1981. In this technique clusters are made by laser vaporization of refractory materials into a pulse of helium or argon in the throat of a supersonic nozzle. The vaporized material nucleates in the gas pulse which then expands supersonically into a vacuum chamber where it cools and is skimmed. The skimmed beam passes into a second chamber where the entrained clusters are ionized by a second laser pulse and the cluster ion mass distributions determined by time of flight mass spectrometry (TOF-MS). The mass spectrum observed by Rohlfing et al.[25] is shown in Figure 4; they pointed out that only ions with *even* numbers of carbon atoms were observable for the new family of clusters with more than 30 carbon atoms. Packing or magic number effects are very weak under these conditions.[27] Bloomfield et al.[28] also studied carbon clusters by the same technique and observed both positive and negative *even* numbered ions. They also studied the fragmentation behavior of the new family and in particular chose the C_{60} cluster for further study and showed that it could be photodecomposed with 532-nm multiphoton laser radiation.

III. The Discovery of C_{60}: Buckminsterfullerene

In September 1985 the reactions of carbon clusters were investigated by the Rice/Sussex group.[3,29,30] These experiments were aimed at simulating the conditions under which carbon nucleates in the atmospheres of cool N-type red giant stars. Circumstantial evidence appeared to suggest[31,32] that such stars might be likely

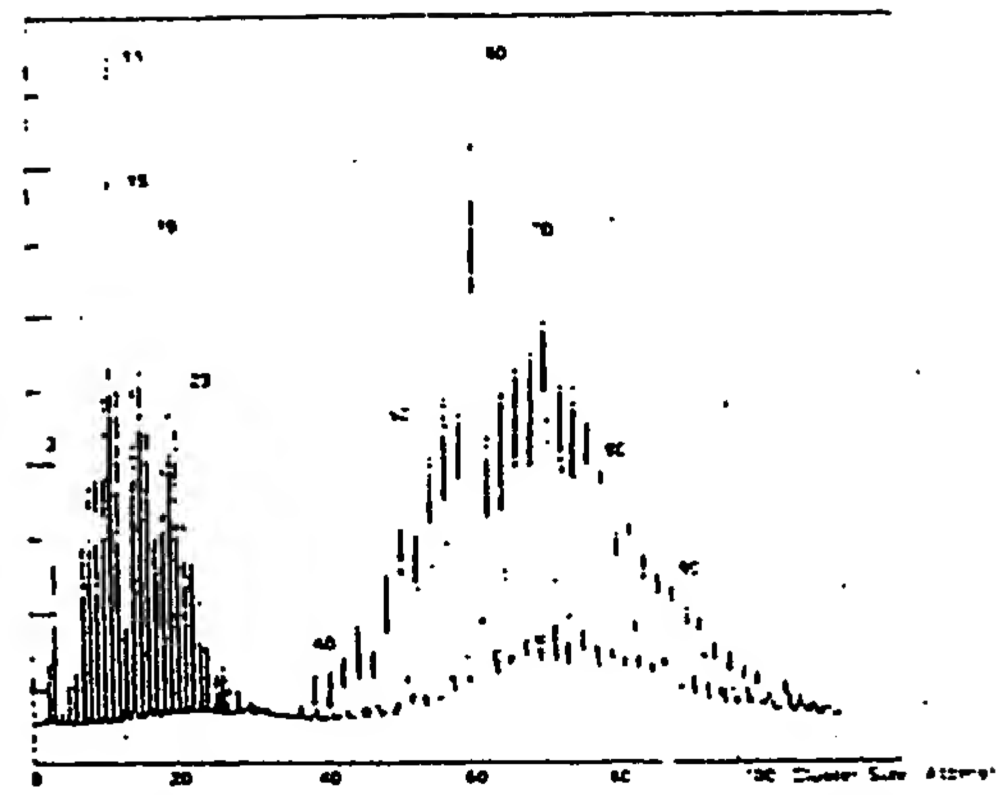

Figure 4. Time-of-flight mass spectrum, observed by Rohlfing, Cox and Kaldor,[25] of carbon clusters produced by laser vaporization of graphite. In this experiment carbon clusters with 30–190 atoms were detected for the first time. These studies showed that only even-numbered clusters were stable (reprinted from ref 25; copyright 1984 the American Institute of Physics).

sources of the long carbon chain molecules in the interstellar medium and in particular that the formation process might be related in some important way to soot formation.[31] The interstellar cyanopolyynes (HC_nN ($n = 5$–11)) were discovered by a synergistic combination of laboratory microwave spectroscopy experiments,[33,34] theoretical analysis,[35] and observational radioastronomy.[36-39] The cluster beam experiments showed convincingly that species such as HC_7N and HC_9N, which had been detected in space,[36-38] could be produced by such laboratory simulations of the conditions in carbon stars.[29,30] A second motivation for probing laser vaporization of graphite was the question of whether carbon clusters were associated with the so-called diffuse interstellar bands as Douglas had proposed in 1977.[40] The development of resonant 2-photon ionization in conjunction with the cluster beam technique to obtain the high-resolution spectrum of SiC_2 by Michalopoulos et al.[41] suggested that the electronic spectra of carbon clusters might be accessible by this technique. During the course of the experiments[29,30] which probed the behavior of the pure carbon clusters a striking discovery was made—under some clustering conditions the 720 mass peak appeared to be extremely strong (Figure 5).[3] Indeed the intensity of the C_{60} peak, relative to the adjacent cluster distribution, could be varied dramatically just by altering the conditions. In particular, conditions could be found for which the mass spectrum was totally dominated by the C_{60} peak—at least in the mass range accessible (Figure 6). It was concluded that C_{60} must be particularly stable to further nucleation and it was proposed that this might be explained by the geodesic factors inherent in a truncated icosahedral cage structure in which all the atoms were connected by sp^2 bonds and the remaining 60 π electrons distributed in such a way that aromatic character appeared highly likely.[3]

In these experiments it was found that the C_{70} peak also showed clear enhancement although to a lesser extent; the C_{60}/C_{70} ratio was ca. 5/1 in general. In previous experiments[25,27,28] the $C_{60}/(C_{58}$ or $C_{62})$ ratio was ca. 2/1 (Figure 4) whereas in the new experiments

1) Used 4th
2) 1k / C_n repeat
3) C_{60} huge
4) C_{70} also

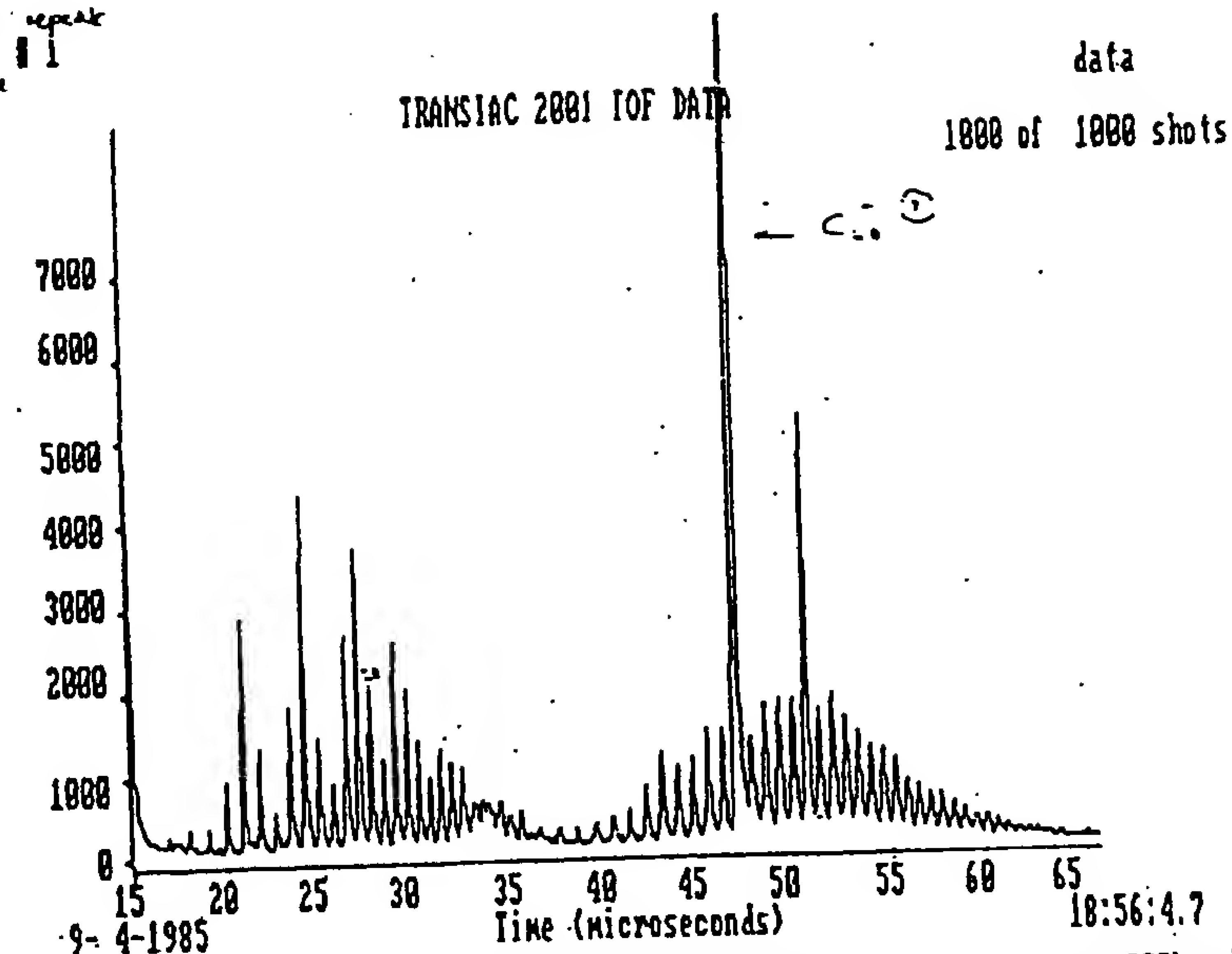

Figure 5. Time-of-flight mass spectrum of carbon clusters produced by laser vaporization of graphite (Sept 4, 1985) under conditions which first exhibited the dominance of the C_{60} cluster and led to the recognition that 60 might be a "magic" number.

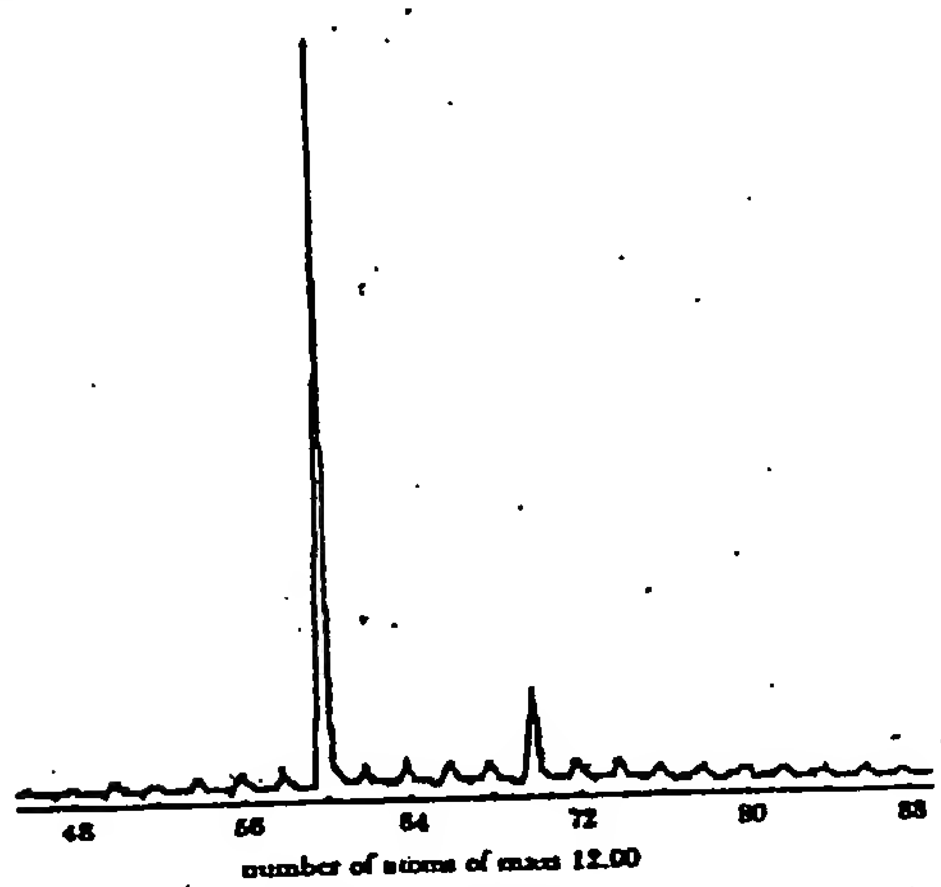

Figure 6. Time-of-flight mass spectrum carbon clusters produced by laser vaporization of graphite under the optimum conditions for observation of a dominant C_{60} cluster signal.[3] Note also the prominence of C_{70}.

conditions were found in which a ratio of 20/1 or more was achieved (Figure 6). It was soon realized that although C_{60} generally appeared fairly special, the conditions under which it appeared dominant were rather unusual. They were conditions in which the major fraction of the carbon had nucleated to form macroscopic particles too large to be detectable by the mass spectrometer. Thus it was recognized that the signal shown in Figure 6 shows the "small" carbon species which remain when the microparticles have formed. Due to the fact that geodesic structural concepts were a guide to the hollow cage structural explanation that

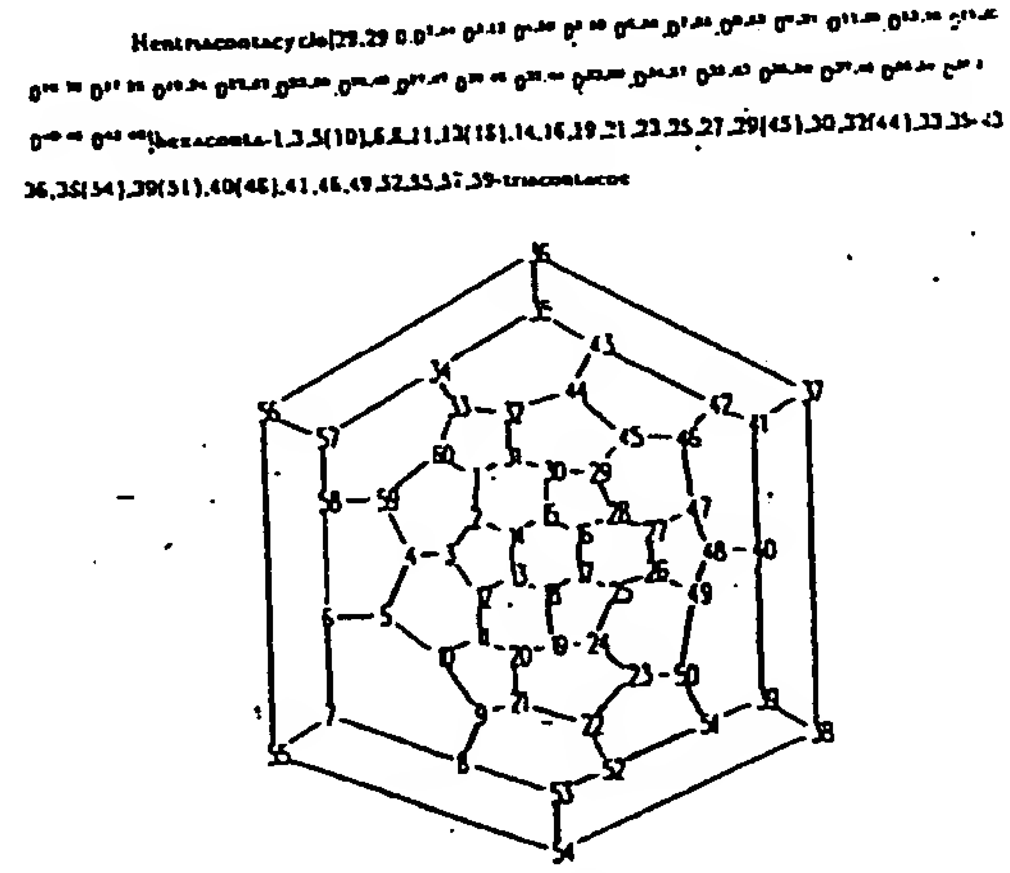

Figure 7. The IUPAC name of fullerene-60 determined by computer analysis—according to P. Rose.[47]

cule was named after Buckminster Fuller, the inventor of the geodesic domes.[43] Although the name chosen, buckminsterfullerene[3,44] is a little long,[45,46] it is not as long as the IUPAC alternative and not as difficult to pronounce (Figure 7)[47] and certainly not as difficult to derive![48,49] The name fullerene can be conveniently and appositely used for the whole family of closed carbon cages with the 12 pentagons and N (other than one) hexagons in an sp^2 network.[3,44] For several reasons, not least the problem of ambiguity with international sports nomenclature, some other names are probably not as satisfactory; they are certainly less enlightening.

Since the buckminsterfullerene detection paper[3] was

work has been carried out. Two complementary accounts covering many of the important general implications and experimental observations have been given by Kroto[50] and Curl and Smalley.[51] More focused accounts have also been published dealing mainly with experimental observations,[52-54] astrophysical implications,[42,55-58] symmetry and structure considerations of fullerene-60, and the icosahedral giant fullerenes.[59,60] The chemical implications have also been discussed by Kroto[61] and Kroto and Walton.[10] Hirota[62] and Heath[63] discuss fullerene-60 as well as other novel carbon molecules.

IV. Sources of C_{60}

In the original work, which showed how conditions could be achieved to produce a signal in which the C_{60} peak was dominant, the pulsed nozzle/laser vaporization technique[26] was used to produce the clusters from a graphite target and photoionization TOF-MS used to detect them. The laser-produced plasma expanded into a high pressure (ca. 1–10 atm) of He and the target graphite surface was continually replenished so that the surface remained essentially flat. A nozzle extender was used to increase the clustering time prior to expansion to ca. 100 μs and the high He pressure increased the nucleation rate. Although initially it was conjectured that perhaps graphitic sheet fragments might have been ablated from the graphite target and rearranged into the buckminsterfullerene structure, subsequent considerations suggested that C_{60} was more likely to have formed by nucleation from carbon vapor consisting, at least initially, of C atoms and very small carbon molecules.[52] Negative ion distributions produced by crossing a laser with the cluster beam just as it exited the nozzle[64] have been studied, and the relationship between these and positive and negative ion distributions obtained directly from the vaporization zone (i.e. without photoionization), has been discussed by Hahn et al.[65] and O'Brien et al.[66] The consensus of opinion was that C_{60} appeared to exhibit special behavior whether charged (positive or negative) or neutral and that the nucleation rate order was neutrals > cations > anions.[66] Very detailed discussion of the conditions under which C_{60} appears to be special has been given by Cox et al.[67] These studies are discussed in more detail in section V.

Carbon cluster distributions exhibiting dominant C_{60}^+ signals, can be produced in another way as O'Keefe, Ross, and Baronavski[68] and Pradel et al.[69] have shown using high vacuum TOF-MS. In these experiments the graphite target is inside the mass spectrometer vacuum system and remains stationary. After several laser pulses a hole is drilled in the graphite and nucleation appears to occur in the cavity. McElvany et al.,[70] using ICR-MS techniques, have shown that if the axis of the laser-drilled hole is aligned parallel to the trapping magnetic field a strong C_{60}^+ signal predominates in the mass spectrum. In a study of the small cluster distribution, McElvany, Dunlap, and O'Keefe[71] found that the vaporization of a diamond target produces the same distribution as does graphite. This result indicates that the clusters appear to be produced by nucleation of atomic/molecular carbon vapor rather by a process involving the ablation of bulk fragments from the target. Meijer and Bethune[72] have modified the original laser

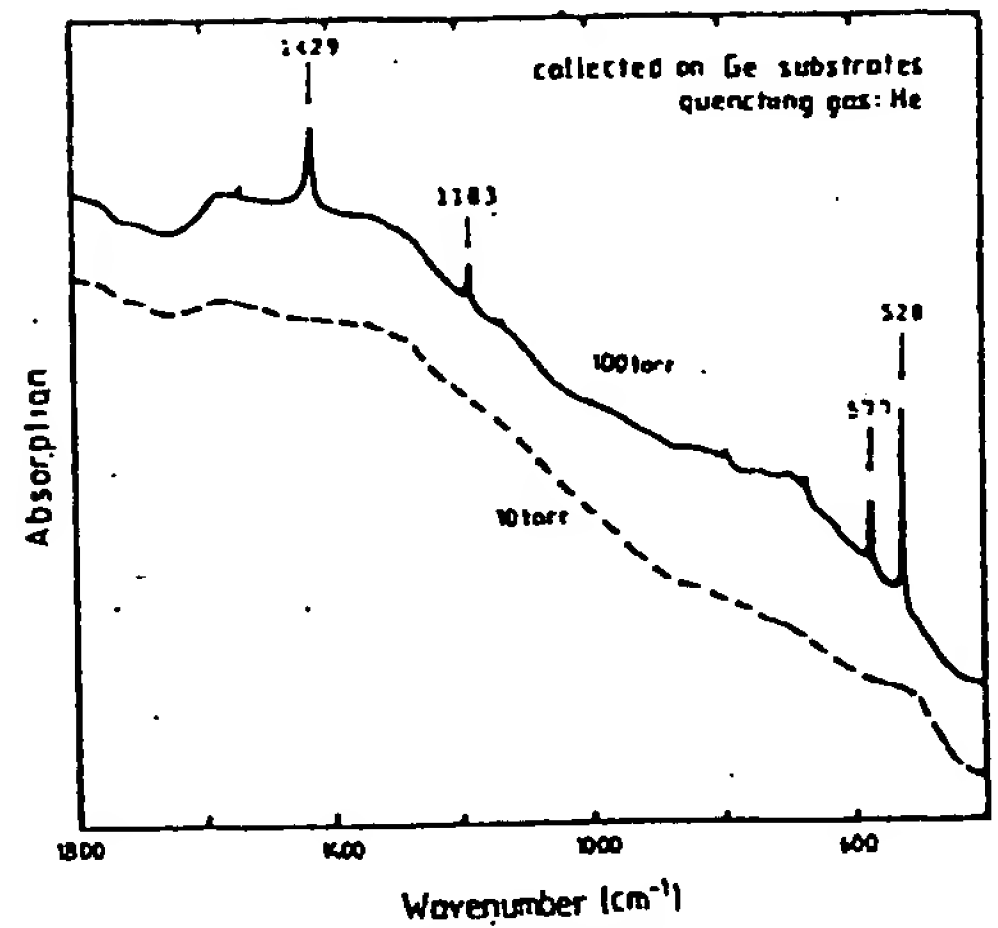

Figure 8. Infrared absorption spectrum observed in 1989 by Krätschmer, Fostiropoulos, and Huffman[5,74] from carbon produced by arc-discharge processing. Krätschmer et al. made the perceptive observation that the four sharp absorption features indicated might belong to fullerene-60. The frequencies were tantalizingly consistent with theoretical predictions (section VIII) for the fundamental vibrations of fullerene-60 (reprinted from ref 74; copyright 1990 Elsevier Science Publishers).

vaporization procedure for producing C_{60}[3] in order to deposit material on a film. They have shown that the mass spectrum obtained by subsequent laser desorption of the resulting material yields a very similar cluster distribution to that of the cluster beam experiments. They have also carried out isotope scrambling measurements[73] supporting the conclusion that C_{60} is assembled from small carbon species in the gas phase after vaporization (see section VI).

A fascinating and ultimately key observation was described in September 1989 by the Heidelberg/Tucson group: Krätschmer, Fostiropoulos, and Huffman[5,74] who detected four weak bands in the infrared spectrum of a film deposited from a carbon arc under argon (Figure 8). Krätschmer et al. pointed out that the vibrational frequencies of the four bands (and associated ^{13}C shifts) observed were in tantalizingly close agreement with theoretical estimates for fullerene-60 (details in sections VIII and IX).

Several other interesting studies have shown that laser vaporization of a wide variety of carbonaceous target materials (other than *pure* carbon) also yields a dominant C_{60} signal: e.g. carbon films (Creasy and Brenna[75]), polymers such as polyimides (Creasy and Brenna,[76] and Cambell et al.[77-79]), coal (Greenwood et al.[80]), polycyclic aromatic hydrocarbons (Giardini-Guidoni et al.,[81] and Lineman et al.[82,83]). Last but not least, So and Wilkins[84] have shown that C_{60} can be detected by laser desorption of soot! In fact they have observed even-numbered carbon clusters with as many as 600 carbon atoms (Figure 9). This result and similar experiments may indicate that giant fullerenes may also be forming.[60] All experiments show that conditions can be found in which the C_{60}^+ peak is either prominent or dominant. However conditions also exist for which this is not the case.[84] It is likely that the availability of many other pathways to "organic" (H-containing species) may be responsible for some of the latter observations

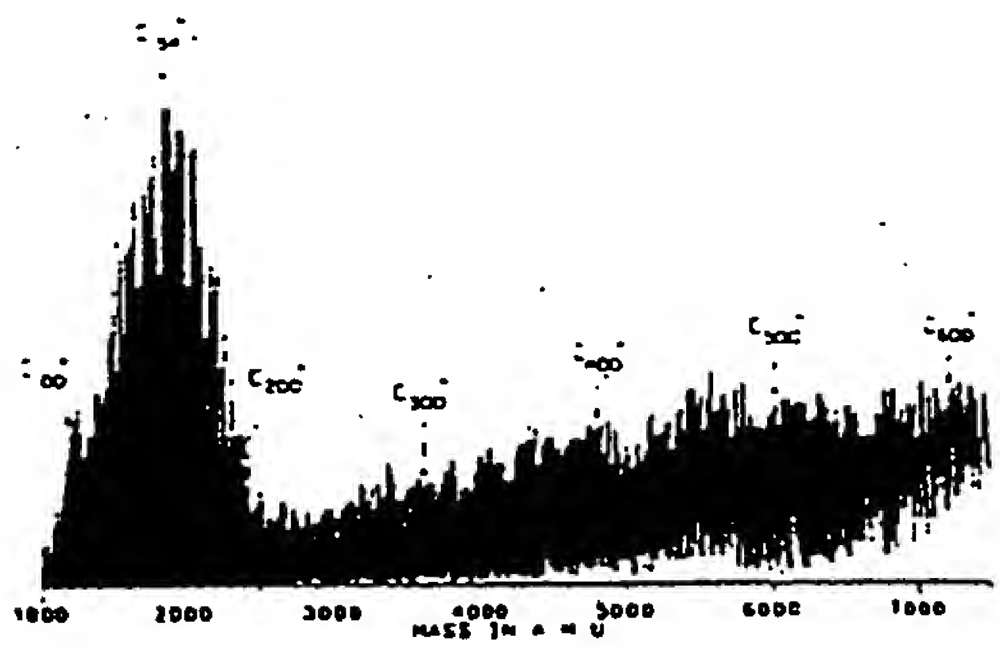

Figure 9. Laser desorption Fourier transform mass spectrum, observed by So and Wilkins,[84] of soot deposited on a KCl-coated stainless steel probe tip. Note that *all* the peaks here also correspond to *even* numbered carbon species. Since only even-numbered carbon aggregates can close perfectly it is possible that the explanation for this phenomenon is that these species are fullerenes and that the larger species are giant fullerenes of the kind depicted in Figure 22.

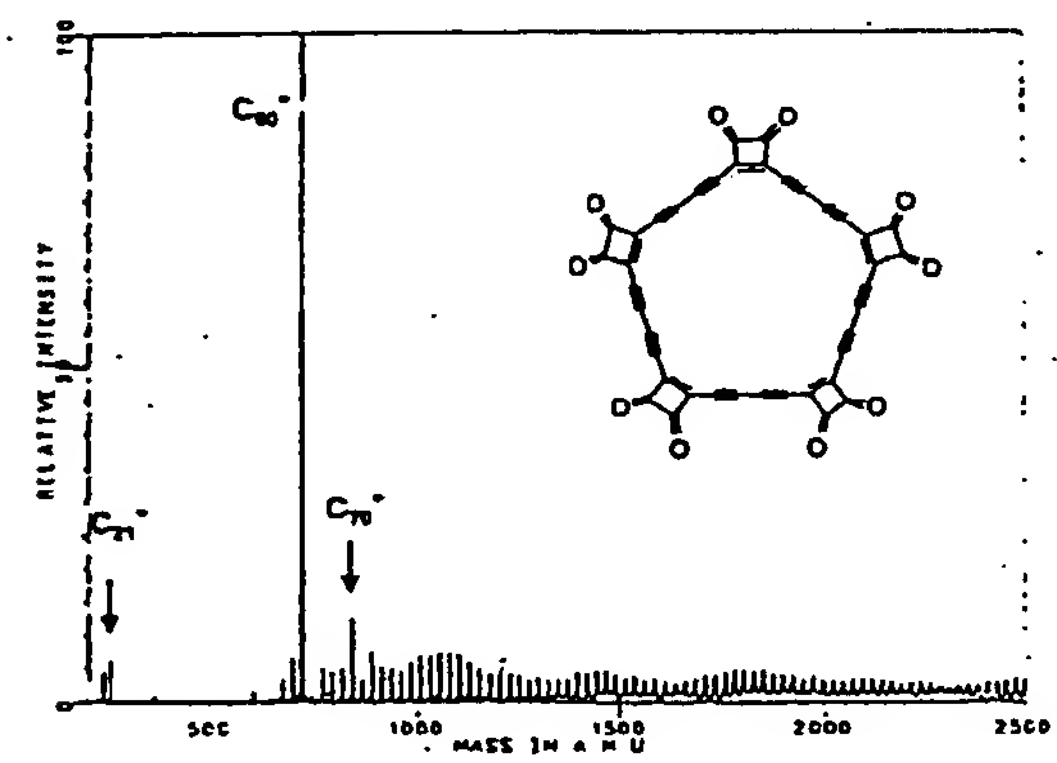

Figure 10. Remarkable positive-ion laser desorption Fourier transform mass spectrum, observed by Rubin et al.,[85] of the ring carbon oxide depicted under low laser power. This oxide which might be expected to decarbonylate to yield a C_{30} monocyclic ring has clearly dimersed to form C_{60} buckminsterfullerene!

A most exciting result was described by Rubin et al.[85] who have used a combination of organic synthesis and laser desorption mass spectrometry. In a preliminary study by the same group (Diederich et al.[86]) attempted to prepare pure carbon rings, a prominent peak for the C_{18} cluster was detected during mass spectrometric analysis of a laser desorbed 18-carbon ring precursor. This work has now been advanced in spectacular fashion; refined measurements on C_{18} and C_{24} precursors[85] yield mass spectra which show prominent C_{60} and C_{70} signals. However most striking is the observation that laser desorption of the C_{30} ring precursor produces a mass spectrum containing a totally dominant C_{60} signal! (Figure 10). This result suggests that, in the vapor phase, a spectacular dimerization process occurs in which two C_{30} polyyne/cumulene rings combine in a concerted folding rearrangement to form the C_{60} cage.[10] The implications of this process and indeed other aspects of the fullerene discovery for organic chemistry have been considered.[10,61]

Some of the most important of all these experiments were those of Homann and co-workers[87-90] who detected

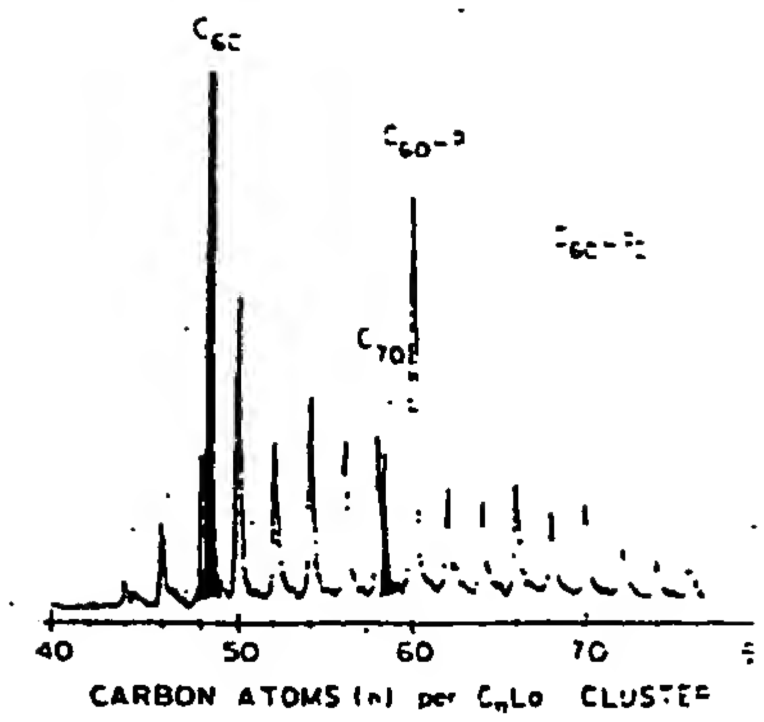

Figure 11. Mass spectrum of C_nLa cluster complexes and bare C_n clusters as observed by Heath et al.[7] when $LaCl_3$-doped graphite is laser vaporized (ArF 6.5 eV, 10 mJ cm⁻¹). Note the particularly strong peak for $C_{60}La$ and the absence of a peak for $C_{60}La_2$. This result is discussed in section VI (adapted from ref 7).

C_{60}^+ in a sooting flame. These observations are discussed in more detail in section VII.

V. Stability and Intrinsic Properties of C_{60}

After the buckminsterfullerene structure was proposed[3] the intrinsic properties of the species were probed by the Rice/Sussex group.[50-54] It was clearly vital to determine how reliable the experimental observation of the "stability" of the C_{60} cluster was, i.e. how "special" or "magic" the cluster actually was and how certain one could be about the buckminsterfullerene hollow cage explanation. After all, the proposal appeared to rest entirely on the observation of a single, strong mass spectrum peak at 720 amu (Figures 5 and 6), and such highly circumstantial evidence needed further support. Mass spectrometry is particularly susceptible to erroneous conclusions drawn on the basis of magic numbers due to the likely presence of ionization and fragmentation artifacts. Various aspects of the original experiment led to the conclusion that the cation mass spectrum (Figures 5 and 6) was most probably an accurate reflection of the neutral cluster distribution. Nevertheless it was necessary to carry out experiments in order to probe the behavior of C_{60} more deeply in order to generate further evidence, albeit still circumstantial, to support the stability conclusion and the cage structure proposal.

During the period from 1985 to 1990 many experiments were performed by a number of groups operating in the cluster field which probed carbon behavior with a view to confirming or falsifying the fullerene-60 proposal. If C_{60} really were a cage then the most obvious next step was to attempt to trap an atom inside the cage. The first result, in this context, was the observation of $C_{60}La$ by Heath et al.[7] By using a graphite disk, soaked in $LaCl_3$ solution a strong signal was obtained for the monolanthanum complex $C_{60}La$, with no evidence of a peak for $C_{60}La_2$ (Figure 11). Cox et al.[91] questioned the conclusion. They pointed out that, since C_{60} needs two 6.4 eV (ArF) photons for ionization and $C_{60}La$ only one, the relative strengths of the $C_{60}La^+$ and bare C_{60}^+ MS signals should not necessarily be taken as reliable gauges of their respective abundances, and a possible $C_{60}La_2^+$ signal might be too weak to detect

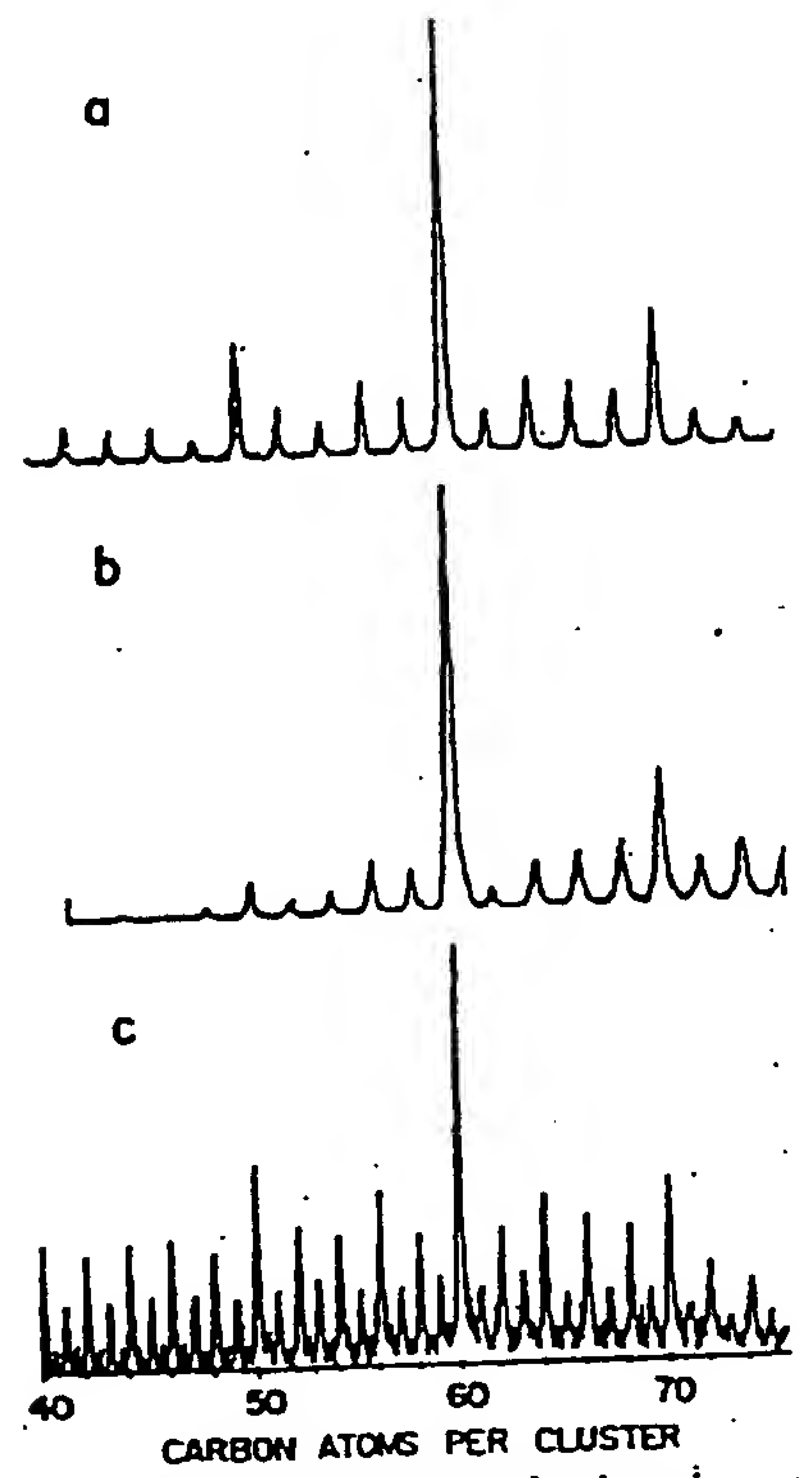

Figure 12. Carbon cluster ions observed under various production conditions:[52] (a) negative ions produced by directing a KrF excimer into the nozzle during expansion, (b) positive carbon cluster ions produced directly during vaporization in the nozzle without the aid of the KrF excimer laser, and (c) negative ions produced directly during vaporization in the nozzle, again without the aid of the KrF excimer laser but with longer residence time in the clustering region than in the case of the positive ions depicted in b (reprinted from ref 52; copyright 1987 Gordon and Breach Science Publishers, Inc.).

Cox et al.[67] have discussed further the cage hypothesis in general and metal atom encapsulation in particular and after detailed assessment they conclude that overall their observations are non-committal over whether C_{60} was a cage or not.

For the smaller carbon species the positive ions display the well known magic numbers: 11, 15, 19, 23 (the so-called "$\Delta n = 4$" effect, cf. Figure 4) whereas the negative ions exhibit a different sequence.[21-24,1,2] The paper announcing the original discovery[3] assumed that the mass spectra (Figures 5 and 6) reflected accurately neutral carbon cluster distributions. If the buckminsterfullerene structural proposal were correct however, the positive and negative ion distributions would be expected to exhibit a similar prominence for the 60-carbon atom analogue. The first experiment to probe this possibility[64] showed that negative ions, produced by laser ionization just after the cluster beam exited from the nozzle exhibited an anion mass spectrum in which C_{60}^- was dominant. In this experiment the neutral species became negatively charged by electron transfer. If the positive or negative ions, produced directly by vaporization are studied, it is found that only after clustering is allowed to continue for a

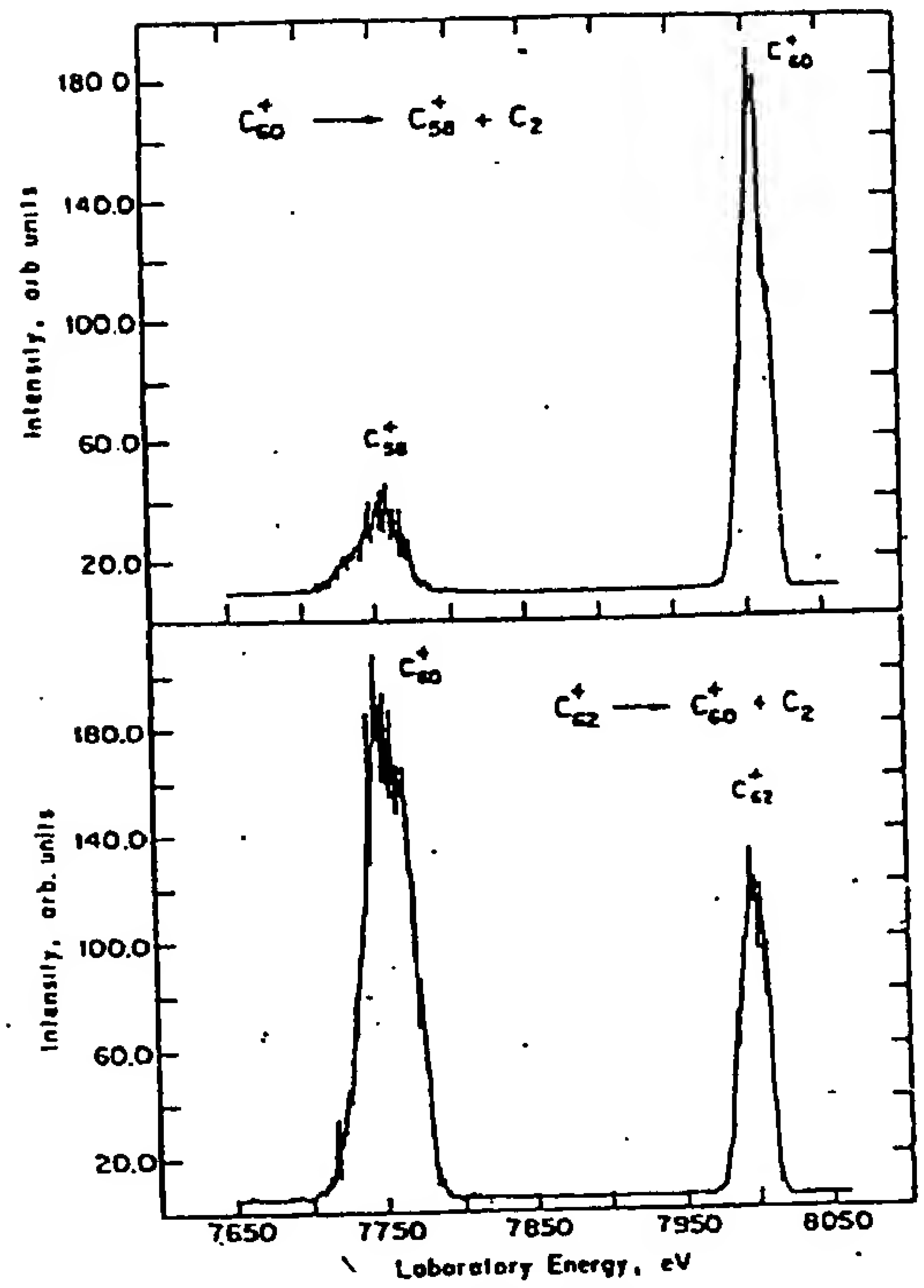

Figure 13. Metastable mass-analyzed ion kinetic energy scans (MIKES) published by Radi et al.[93] The parent ion (on the right) is mass selected by the magnetic analyzer and the horizontal axis is a scan of the electrostatic analyzer voltage. The parent ion energy is 8 keV. C_2 loss is observed from C_{60}^+ (above) and C_{62}^+ (below). Note the dramatic differences in metastable activity as reflected by the relative intensities of the product peaks, relative to their parent ions in these two cases (reprinted from ref 93; copyright 1990 the American Institute of Physics).

significant length of time is the C_{60}^- anion dominant[66] otherwise it is not.[65] Some examples of mass spectra recorded under various conditions[51,64,66] are presented in Figure 12. Cox, Reichmann, and Kaldor[67] describe some intriguing relative time-of-flight differences in behavior between various individual clusters, in particular C_{28} and C_{60}, which are highly dependent on the nozzle parameters. These experiments appear to suggest that wall reactions may occur in the nucleation channel. It is possible that what was observed in this experiment was C_{60} deposited in the channel which subsequently desorbed. The main evidence for the importance of wall effects lies in the detection of $C_{60}K$ clusters when a new, pure (i.e. K free) carbon target replaces a previous one doped with potassium.

Important observations have had a bearing on the stability of C_{60}. The very early experiments by Bloomfield et al.[28] showed that C_{60} was susceptible to multiphoton fragmentation. A series of studies by Bowers and co-workers[92-94] showed that C_{60} could undergo metastable fragmentation. Particularly interesting is the observation that C_{60} exhibits much lower metastability than other neighboring clusters such as C_{62} as shown in Figure 13. These results suggest that hot C_{60} may exhibit phenomena associated with fluidity—perhaps an intriguing form of surface fluidity. On the

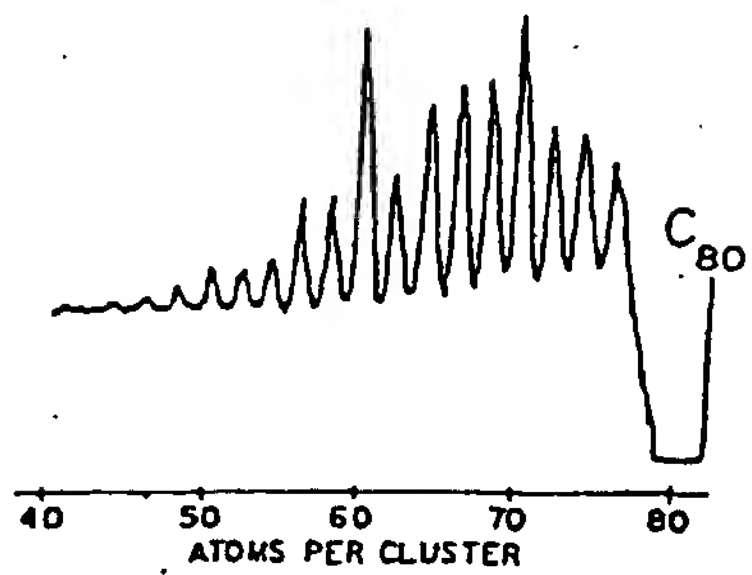

Figure 14. Fragmentation products under ArF (15 mJ cm^{-2}) irradiation observed by O'Brien et al.[95] Under irradiation the mass selected C_{80}^+ cluster (including ca. 20% C_{78} and ca. 10% C_{82}) is here seen to fragment into smaller even clusters: C_{78}, C_{76}, etc. by loss of C_2, C_4, etc. Particularly interesting is the observation that C_{60} and C_{70} are favored fragmentation products (reprinted from ref 95; copyright 1988 the American Institute of Physics).

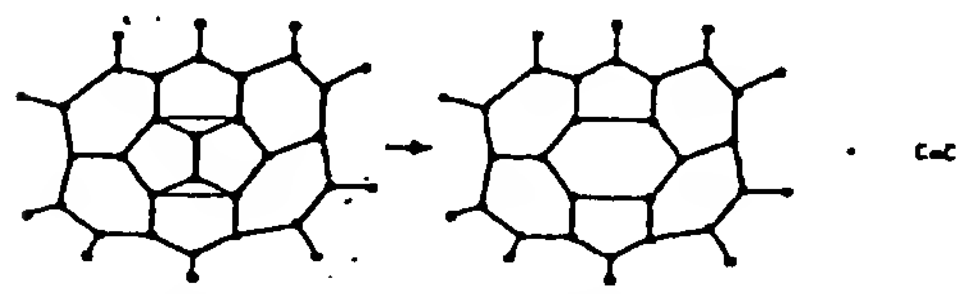

Figure 15. Hypothetical fragmentation–rearrangement mechanism presented by O'Brien et al.,[95] involving C_2 loss and cage re-sealing which could explain the fragmentation phenomena in Figure 14 (reprinted from ref 95; copyright 1988 the American Institute of Physics).

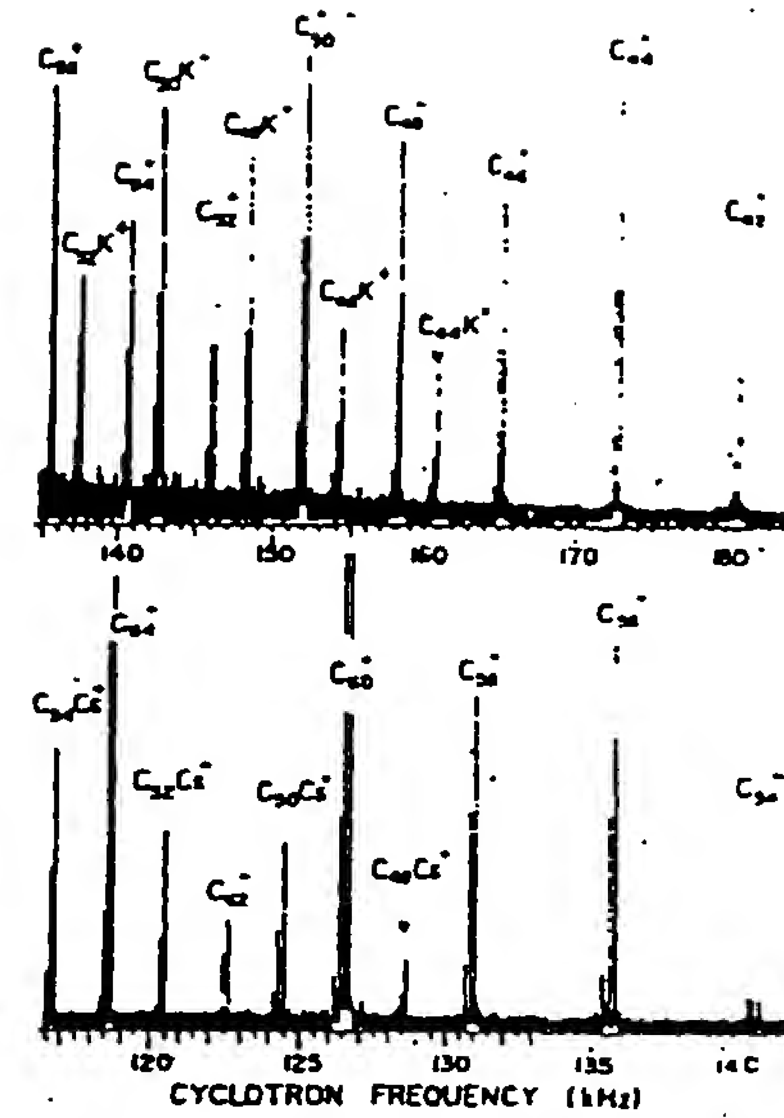

Figure 16. High-order photofragmentation pattern of $C_{60}K^+$ (above) and $C_{60}Cs^+$ (below) detected by FT-ICR mass spectrometry by Weiss et al.[96] The break-offs observed at $C_{48}Cs^+$ and $C_{44}K^+$ are in excellent agreement with expectation for the smallest fullerene networks capable of encapsulating the metals, based on the known ionic radii (reprinted from ref 96; copyright 1988 American Chemical Society).

other hand, O'Brien et al.[95] and Weiss et al.[96] have shown that cold C_{60}^+ exhibits little, if any, evidence for fragmentation. The likely explanation for this disparity is that clusters produced under the vacuum vaporization conditions[28,92-94] possess massive amounts of internal energy leading to metastable C_{60}^+. As special behavior is most dramatic after extensive degrees of nucleation have occurred it is possible that the C_{60} signal observed under vacuum ablation conditions is actually a mixture of isomers, at least in part. Related studies by Hasselberger et al.[78] show that metastable fragmentation is less severe when clusters are produced with lower internal energies. The measurements of O'Brien et al.[95] showed that multiphoton fragmentation of clusters with 32–80 atoms occurred by elimination of even carbon fragments, C_n (n = 2, 4, 6, ...), rather than lower energy C_3 species. Particularly intriguing is the observation that large clusters, with 70 or more atoms fragment to form smaller even-cluster distributions in which C_{60} is special (Figure 14). Clusters with less than 32 atoms fragment into a range of smaller carbon species, a result interpreted as evidence that clusters with less than 32 atoms were not cages. O'Brien et al.[95] also presented an interesting mechanism for this process which is depicted in Figure 15. Laser irradiation studies by Weiss et al.[96] showed that the metal complexes were also quite resistant to photofragmentation. They also showed that multiphoton fragmentation of $C_{60}M^+$ resulted in metal-complex products C_nM^+ for which the critical smallest sizes occur at n = 48, 44, 44–42 for M = Cs, K, and La, respectively (Figure 16). This result provided strong circumstantial evidence for metal atom encapsulation because the minimum physical cage size scales with the ionic radius of the metals in the series.

Prior to the isolation of macroscopic samples of the fullerenes (section IX) several experiments were carried out in order to determine their physical, mainly spectroscopic, properties. Tandem TOF-MS experiments were devised to explore the possibility that the spectra of C_{60} (neutral) and C_{60}^+ (the positive ion) might be responsible for the astrophysically intriguing diffuse interstellar bands (section XI). These experiments involved the resonant photodissociation of a van der Waals complex of benzene with neutral C_{60} and C_{60}^+. It proved possible to photofragment C_{60}-C_6H_6 but not the ion complex, C_{60}^+-C_6H_6, probably because charge transfer forces bind the adduct too tightly in the ion complex.[97] Very weak photofragmentation of the neutral complexes of C_{60} with C_6H_6 and CH_2Cl_2 was observed at 3860 Å by depletion spectroscopy.[98]

Yang et al.[99] used an ingenious technique developed by Cheshnovsky et al.[100] to observe the UV photoelectron spectra of negative cluster ions. In these experiments the spectra of carbon clusters from C_{48} to C_{84} have been observed. Of particular interest are the UPS patterns of C_{50}, C_{60}, and C_{70} which show a low energy LUMO feature consistent with closed shells for the neutral species. C_{60} had the lowest electron affinity: viz 2.6–2.8 eV. These observations provided further strong support for the fullerene proposal. The ionization potential of C_{60} was obtained in an elegant way by Zimmerman et al.[101,102] who used a series of charge transfer measurements with various reactants of known IP to bracket the IP of C_{60}: 7.61 ± 0.11 eV. This result was consistent with conclusions drawn from early experiments which indicated that the IP lay between the energy of the ArF excimer laser (6.4 eV) and that of the F_2 laser (7.9 eV) because C_{60} was 2-photon ionized b...

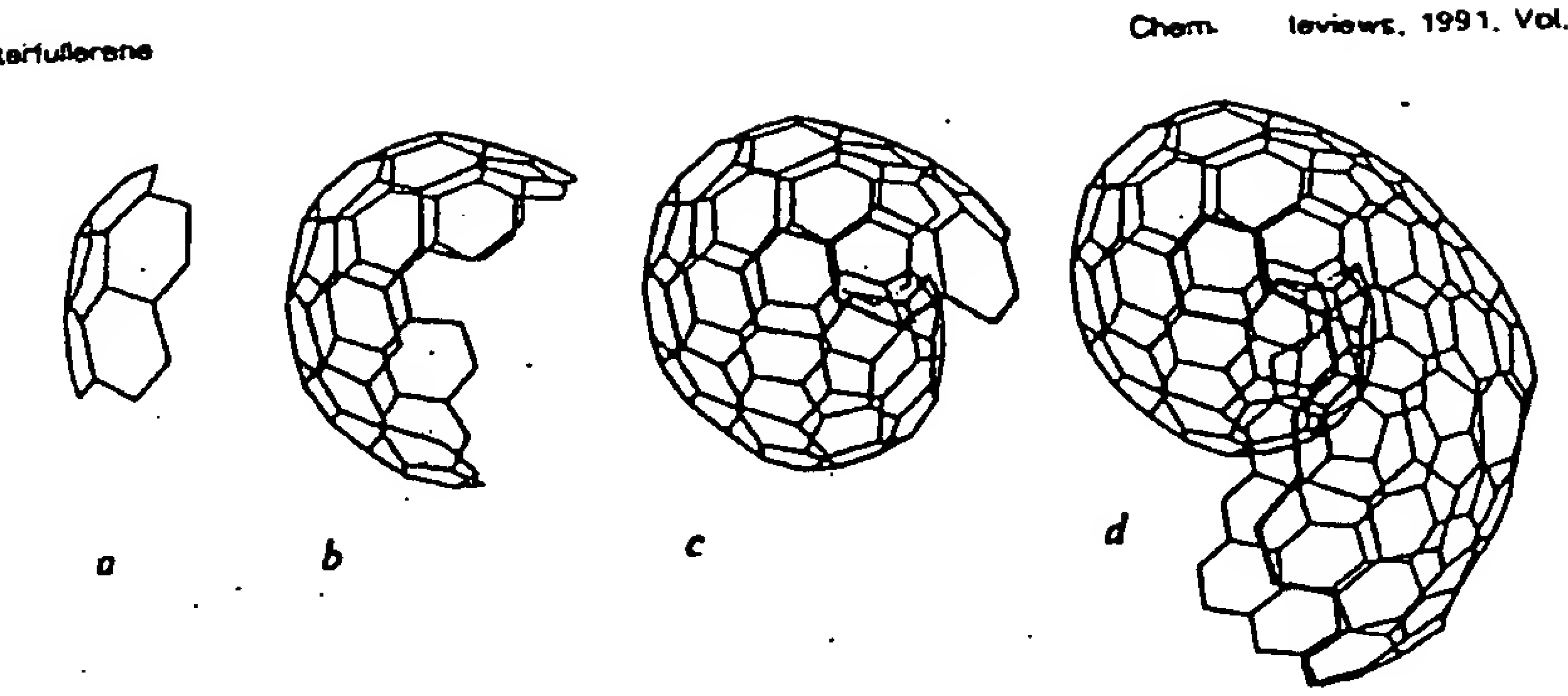

Figure 17. Diagramatic representation[108] of a hypothetical carbon vapor nucleation scheme[103,108] proposed for the formation of concentric shell graphite microparticles. Note that the structure c has overlapped and so trapped the trailing edge inside the spiraling network. This species is thus essentially the embryo for further growth. It is proposed that C_{60} might be produced by a modification of this process in which the edges meet and seal to form a closed cage. In such a case further growth by chemical bond formation might be expected to be halted. It was conjectured that similar structures might occur as intermediates during soot nucleation (reprinted from ref 108; copyright 1988 Macmillan Magazines Ltd.).

ArF and 1-photon ionized by F_2.[103,67]

As mentioned in section IV, the most intriguing and convincing spectra were those obtained in the infrared study of Krätschmer, Fostiropoulos, and Huffman in 1990[5,74] (see further details in sections VIII and IX).

VI. Reaction Studies

The first reaction studies aimed at probing the cage concept were those of Heath et al.[7] and Cox et al.[91,67] (discussed in section V) who studied the carbon/metal complexes. Rohlfing et al.[25] and Heath et al.[29,30] carried out similar reaction studies which focused mainly on the properties of the carbon chains. It is also important to note that van der Waals complexes can form in the supersonic beam if C_{60} is cold.

When various gases such as CO, NO, and SO_2 were introduced into a reactor, placed downstream from the nozzle in which C_{60} is formed, Zhang et al.[103] showed that all the even carbon clusters were totally unreactive. The odd clusters were, on the other hand, very reactive. These experiments gained significant further support from the studies of McElvany et al.[70] and Weiss et al.[96] which showed C_{60} and its analogues to be extremely unreactive in an ICR trap. However if gases are mixed with the driver gas in the nozzle, reactions can take place before and after C_{60} is formed. With hydrogen, a wide range of hydrocarbon products is detected (Rohlfing,[104] Hallett et al.,[105] and Doverstal et al.[106]). Rohlfing has used an in-line reflectron modification of the cluster beam technique and made some very careful high-resolution mass spectrometric measurements of the reactions of clusters C_{20}–C_{80} with hydrogen.[104] The variations in reactivity appear to be structure related and consistent with the cage proposal. The study suggests that chain cluster species with as many as 44 carbon atoms may be present. Complementary experiments by Hallett et al.[105] and Doverstal et al.[106] indicate that clusters in the C_{20}–C_{40} range show at least three different types of reactivity as evidenced by the mass spectrometric patterns of the hydrogenated products. The observations[106] are consistent with the proposal that small fullerenes (C_{20}, C_{24}, C_{28}, C_{32}, C_{50}) can form.[8] They are also consistent with the fact that formation that no 22 atom fullerene can exist, as pointed out by Fowler and Steer.[107]

VII. Gas-Phase Carbon Nucleation and C_{60} Formation

It would appear that most workers in the field are able to observe special behavior fairly easily and under a wide range of conditions, all of which have one major feature in common: C_{60} appears to be dominant *only* when nucleation nears completion, leaving behind C_{60} and other even-numbered relatives such as C_{70}. This result has one obviously simple explanation; at least some fraction of the even clusters—particularly C_{60}—is unreactive toward growth into macroscopic particles. The spontaneous creation of C_{60} requires a mechanistic explanation. In particular, entropy factors clearly need to be carefully assessed when it is proposed that so symmetric an object is formed in a chaotic plasma. A feasible nucleation mechanism was provided by Zhang et al.[103] and refined further by Kroto and McKay.[108] The nucleation model proposes that curved sp^2-linked (aromatic) carbon networks form (Figure 17) and can serve as embryos for further growth. The energetics of sheet carbon cluster radicals is invoked to explain the curvature/partial closure. Essentially the drive toward closure is governed by the energy released as a result of eliminating the edge dangling bonds. For instance a flat graphite-like sheet of 60 atoms would have at least 20 dangling bonds, whereas fullerene-60 would, of course, have none. In general, in a chaotic system, partly closed, overlapped embryos, such as that shown in Figure 16c, are expected to form and which, once overlapped, cannot close perfectly. These species are probably highly active nucleation sites to which permanent chemical binding of adsorbing fragments can take place. Of course some form of closure/annealing process might take place if the temperature is high enough for intra and extra network rearrangement to occur. It was proposed[103,108] that during this general spiral nucleation process some embryos would close forming fullerenes, particularly fullerene-60 which would no longer present a site for efficient accretion. The process is primarily a physicochemical nucleation scheme in which the fullerenes act as deadends for the most rapid nucleation.

After embryo formation, epitaxial growth has been shown to result in icospiral graphitic giant molecules or microparticles[108] with structures consistent with

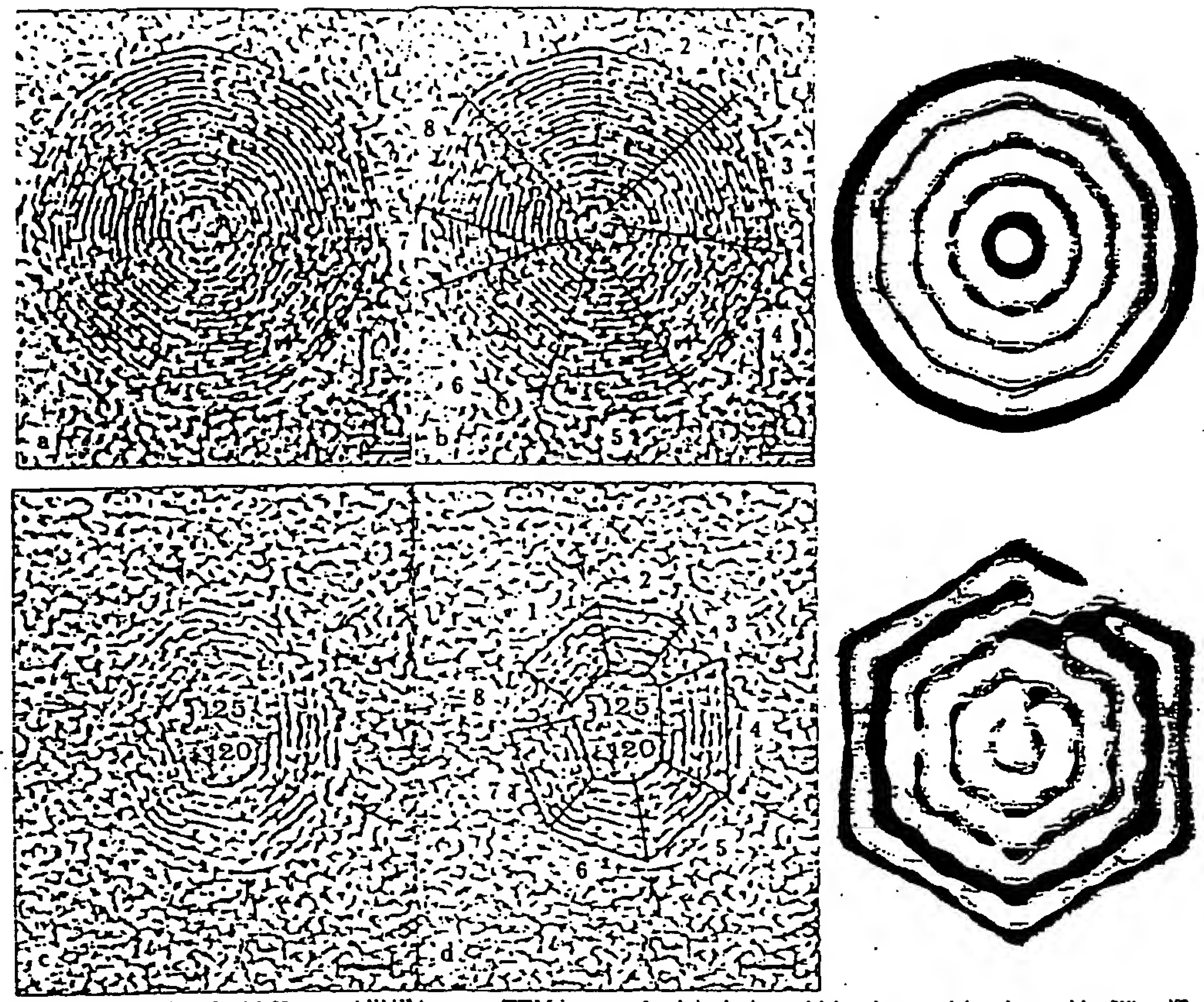

Figure 18. Comparison by McKay et al.[111,112] between TEM images of polyhedral graphitic microparticles observed by Iijima[109] and simulated TEM images for a hypothetical spiral shell particle predicted by the nucleation scheme depicted in Figure 17. The fairly round particle observed by Iijima which is depicted in a and b is seen to exhibit a similar pattern to the simulation top right. On the other hand the more polygonal particle, shown in c and d, exhibits a similar pattern to the simulation shown bottom right. The simulations are for the same particle observed from different angles. The hypothetical particle has shell interconnections which can most easily be seen in the lower right simulation. In b and d the polygonal outlines are delineated.

those of spheroidal graphitic microparticles observed by Iijima in 1980.[109,110] Kroto et al.[111,112] have provided further support for the scheme in the form of TEM image simulations based on the icospiral concentric shell structure concept,[108] in excellent agreement with the Iijima images as depicted in Figure 18. Roulston et al.[113] have shown that certain electronic and structural properties of amorphous semiconducting carbons can be explained on the basis of a spheroidal graphitic infrastructure, rather than by the traditional flat microstructure. Yacaman et al.[114,115] have shown that FT power-spectra processed, electron microscope images of carbon microparticles appear to be consistent with the quasiicosahedral spiral substructure.[108] Attention has been drawn to the fact that small graphitic microparticles actually consist of crystalline quasiicosahedral graphitic cores surrounded by amorphous carbon surface layers.[116,109] Interestingly, Iijima[110] has shown that the TEM structure at the nucleus of one of the carbon microparticles, studied earlier[108] was consistent with the image expected if it were a C_{60} cage. With hindsight this result demands further serious investigation to see whether fullerene-60 can itself be encapsulated during later stages of particle growth.

Wales[117] has considered some statistical aspects of the growth dynamics of closed-cage structures and Bernholc and Phillips have discussed the kinetic factors involved in the growth of carbon clusters in general.[118]

It was also suggested that a modified form of the nucleation scheme, devised to account for the spontaneous creation of C_{60}, could also explain the spheroidal nature of soot.[103,108,50,51,119] This proposal was criticized by Frenklach, Ebert, and co-workers[120-123] who favor an earlier theory, which invokes the physical condensation of flat PAH molecules held together by van der Waals forces into coagulating liquid drops. However, Harris and Weiner point out how little has been firmly established about the soot formation mechanism.[124] It can in fact be demonstrated[125] that the new scheme is broadly consistent with kinetic, structural, and chemical observations made on soot and its formation process.

The new nucleation scheme predicts that some C_{60} should form as a byproduct[103,108] of soot production. Subsequently Gerhardt, Löffler and Homann,[87-90] in studies of the ions produced in a sooting flame, found conditions under which the mass spectrum shown in

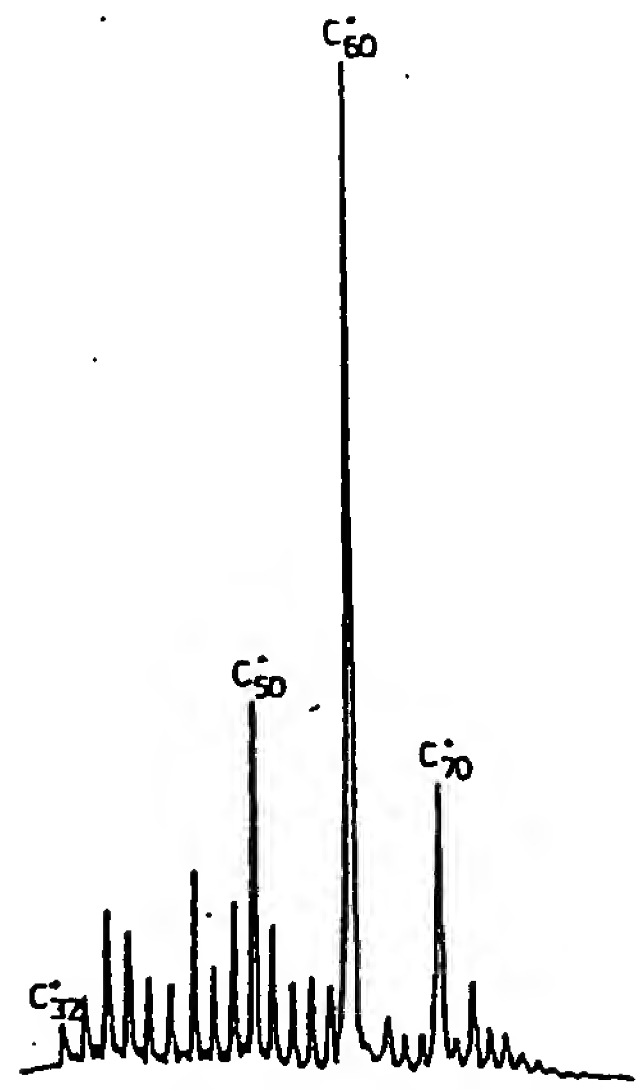

Figure 19. Mass spectrum, observed by Gerhardt, Löffler, and Homann,[87-90] of positive ions produced by a sooting benzene/oxygen flame (C/O = 0.76) (reprinted from ref 87; copyright 1987 Elsevier Science Publishers).

Figure 19 is obtained. This spectrum is almost identical with that observed during the pure carbon laser vaporization experiments where C_{60}^+ is the dominant ion! Homann and co-workers conclude that this observation should not be taken as support for the new spiral nucleation scenario as the tell-tale even ions with a dominant C_{60}^+ peak are not seen until after the inception of soot particle formation. The carbon/hydrogen reaction studies[104-106] promise to shed further light on the soot formation process, but the way in which the results might dovetail with the conventional data remains to be ascertained. Kroto has summarized the present state of affairs from this viewpoint.[125]

VIII. Theoretical Studies of the Fullerenes

Theoretical studies predating the discovery of C_{60} have been discussed in section II. After the discovery, theoreticians had a ball and many aspects of the molecule's properties have already been probed. The comprehensive overview of theoretical work on fullerene-60 presented by Weltner and Van Zee[2] is here conflated with more recent work.

One important aspect of the original experimental observations was the fact that C_{70} *also* showed special behavior. Topological and chemical stability arguments, as discussed by Kroto[8] and Schmalz et al.,[9] explain this observation as being entirely consistent with the fullerene proposal. Indeed these studies suggested that if the C_{60} mass spectrometric signal were due to its having a closed cage fullerene structure, C_{70} should show special behavior also, for the same reason. Thus most importantly and rather convincingly, the fullerene structure proposal no longer rested on the single line observation. In fact it had now gained significant further support by the fact that a prediction had been made and neatly confirmed. Indeed the two observations, taken together, provided convincing evidence for the existence of a whole family of fullerenes and further probing suggested that in addition to C_{60} and C_{70}, the C_{24}, C_{28}, C_{32}, and C_{50} clusters (Figure 20) should also show varying degrees of special stability[8,9] (N.B. fullerene-22 cannot exist[107]).

The dominance of C_{60} and C_{70} was ascribed to the fact that these are the smallest fullerenes that can have an isomer (one in each case) in which none of the 12 pentagonal configurations, necessary and sufficient for closure, abut.[8,9] It was shown[8,50] that the predictions were commensurate with the mass spectrum obtained by Cox et al.[67] (Figure 21) and consequently there existed convincing experimental evidence for the fullerene *family* proposal. Since even-numbered carbon clusters are detectable with as many as 600 or more carbon atoms,[84] the possibility of giant fullerenes[108,126] such as C_{240} and C_{540} shown in Figure 22 appears to be an exciting possibility.[60]

Isomer stability has been discussed by Stone and Wales[127] who noted that the difference in energy between isomers is small and suggested that the C_{60} signal should be due to a mixture of isomers. This result is difficult to reconcile with the observation (Figures 5 and 6) since it leads to the conclusion that C_{60} is no more special than other clusters such as C_{62}. Potential energy functions have now been developed for the carbon cages systems by Takai et al.[128] and Balm et al.[129] The simulated annealing, Monte-Carlo methods used by Zerbetto[130] to study the behavior of small carbon clusters have been applied by Ballone and Milani[131] in order to show that the fullerene cages are minimum energy structures.

A group theoretical analysis of the electronic properties of the fullerene family, by Fowler and Steer,[107] showed that the members, C_n where $n = 60 + 6k$ (k = 0, 2, 3, 4, ..., i.e. an integer other than one), should have closed-shell electronic structures. The degree of aromaticity in a compound is of interest, and the number of Kekulé structures is often considered to be a guide. A total of 12500 for fullerene-60 has been calculated

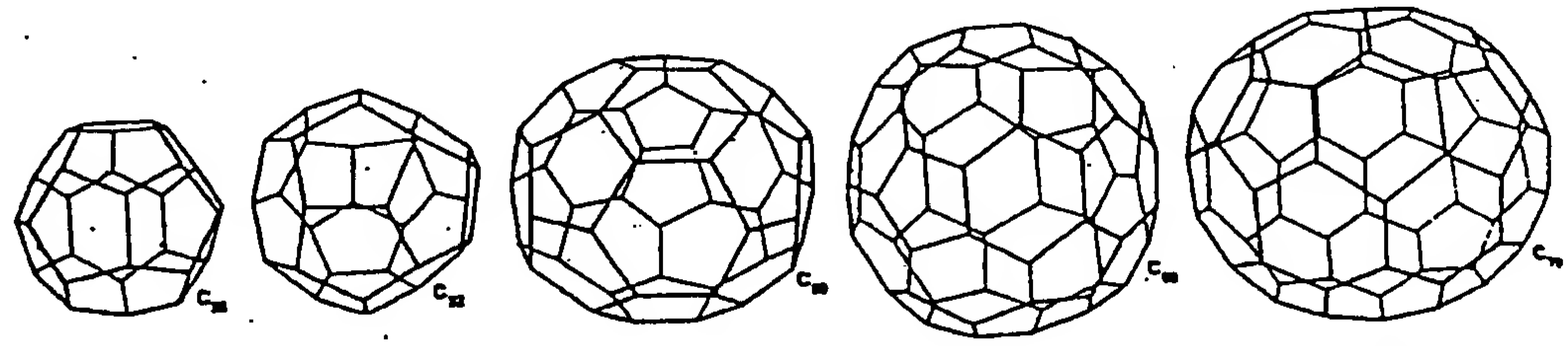

Figure 20. Five possible "magic" fullerenes predicted to display enhanced stability, relative to others in the range with 20–80 atoms, on the basis of chemical and geodesic factors[8] (reprinted from ref 8; copyright 1987 Macmillan Magazines Ltd.)

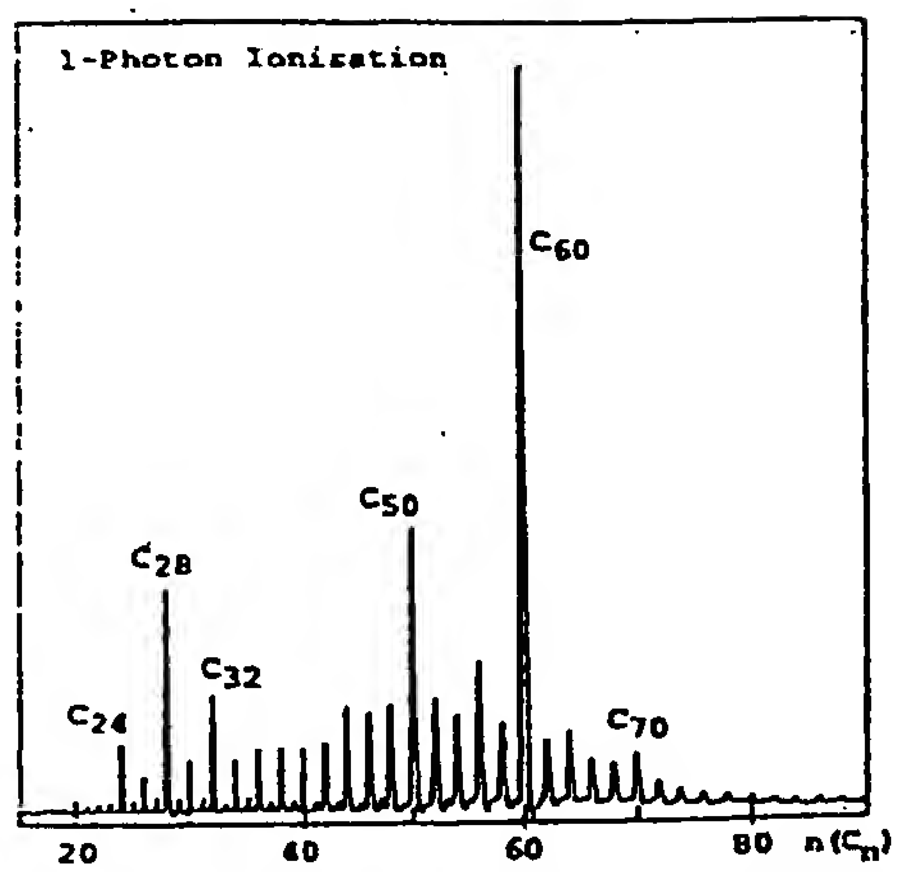

Figure 21. Time-of-flight mass spectrum taken from the data of Cox, Reichmann, and Kaldor.[67] The strong peaks are in excellent agreement with expectation[8,9] if they correspond to fullerenes. The fullerenes 24, 28, 32, 50, 60, and 70 (Figure 20) are predicted to exhibit enhanced stability, i.e. are magic. Note the sharp cutoff at C_{24} which is consistent with the fact that a no 22 atom fullerene can form.

by Schmalz et al.,[132] Hosoya,[133] Brendsdal and Cyvin,[134] and by Elser.[135] Resonance circuit theory has been applied to this problem by Schmalz et al.,[132,9] Klein et al.,[136,137] as well as Randic, Nikolic, and Trinajstic.[138–140] These studies indicate that account must be taken of the fact that some resonance structures make negative contributions to the aromatic stabilization. Schmalz et al.[9] compared resonance circuit theory with Hückel molecular orbital (HMO) theory and concluded that C_{60} should be less aromatic than benzene. Amic and Trinajstic[140] discuss stabilization arising from bond delocalization. Graph theory has been applied to C_{60} and to other systems by Balasubramanian and Liu[141,142] and also by Dias who has circumvented group theory in order to simplify Hückel calculations.[143] Hückel calculations on fullerene-60 have been made by Haymet[144,20] and the stabilization due to delocalization discussed. Jiang and Zhang[145] have calculated the stability of fullerene-60 by Hückel theory using moment analysis techniques. Hess and Schaad[146] as well as Aihara and Hosoya[147] have also applied Hückel theory to the problem, focusing on aspects of spheroidal aromaticity.

Fowler and Woolrich[148] have made three-dimensional HMO calculations which predict that C_{60} and C_{70} are closed shell systems. Fowler[149] extended this approach in order to assess the stability in other, larger fullerene cages, while Fowler, Cremona, and Steer[150] have discussed bonding in nonicosahedral spheroidal fullerene cages. Fowler[151] has extended these ideas to various classes of cylindrical fullerenes and predicted closed electronic shells with an empty nonbonding orbital for clusters consisting of $10(7 + 3k)$ and $12(7 + 3k)$ atoms with 5- and 6-fold symmetry. Ceulemans and Fowler[152,153] considered possible Jahn–Teller distortion pathways for icosahedral molecules.

Byers Brown[154] has discussed the simplification that high symmetry imparts to π-system calculations and obtained algebraic solutions for the orbital energies of fullerene-60. Electronic and vibrational properties were calculated by using a two-dimensional HMO method by Coulombeau and Rassat.[155] Semiempirical calculations including the effects of nonplanar π-orbital overlap due to curvature have also been carried out by using the free-electron model in the Coulson–Golubiewski, self-consistent Hückel approximation by Ozaki and Takahashi.[156] Haddon et al.[157,158] have also considered the effects of nonplanarity, i.e. pyramidalization.

Extended Hückel calculations by Bochvar, Gal'pern, and Stankevich[159] and INDO and INDO/CI calculations by Feng et al.[160] have been applied to C_{60} and its isomers. A comparison between C_{60} and graphite was made by MNDO with geometry optimization by Newton and Stanton.[161] McKee and Herndon[162] also applied MNDO theory to cage carbons and concluded that the flat "graphitene" cage,[144] in which two coronene sheets are linked by pentagonal rings at the edge to form a disk-like structure should be more stable than fullerene-60. These authors also considered the mechanism of formation arising from rearrangement. Rehybridization and bonding were studied by Haddon, Brus, and Raghavachari who applied the π-orbital axis vector/3d-HMO (POAV/3D HMO) method[157,158] and concluded that larger clusters were favored. It was also postulated that fullerene-240 should be more stable than C_{60}. Lüthi and Almlöf[163–165] have carried out

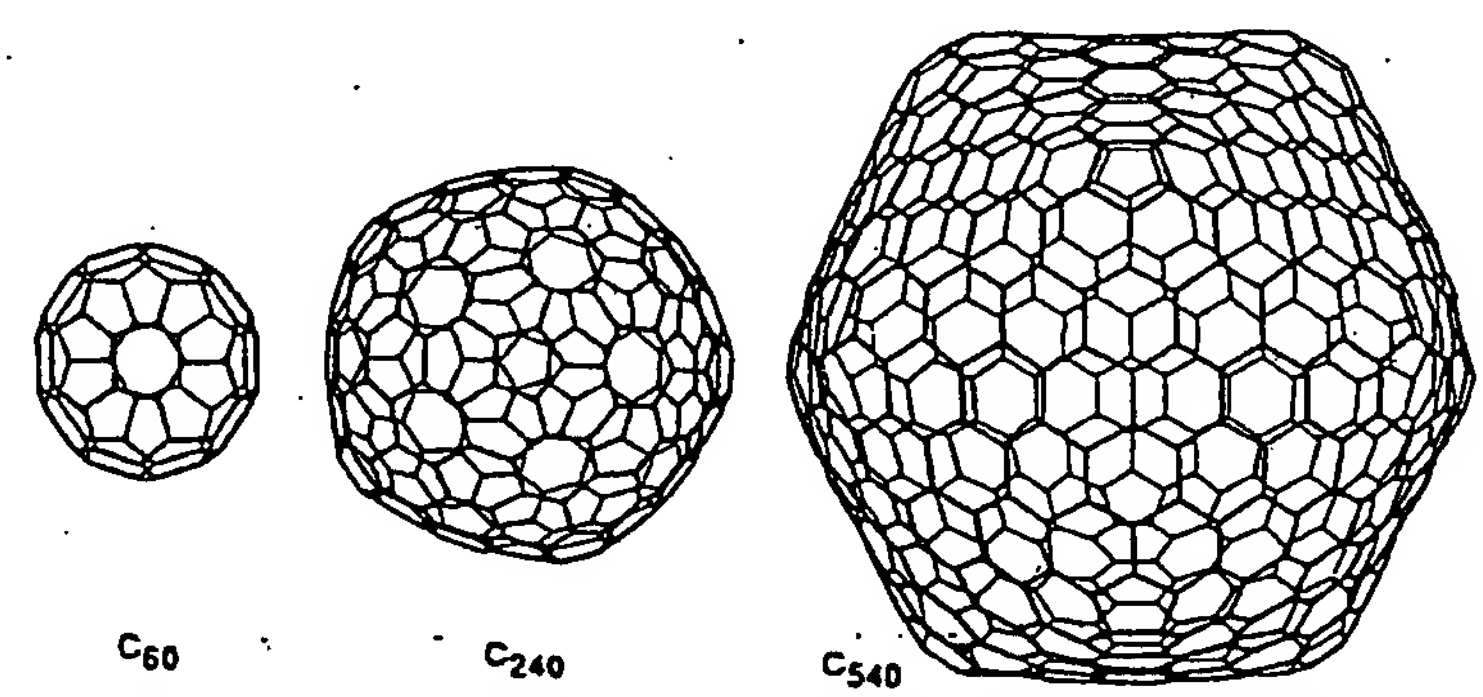

Figure 22. The set of fullerenes C_{60}, C_{240}, and C_{540} with diameters in the ratio 1:2:3. Kroto and McKay[108] showed that quasiicosahedral shape develops rapidly for the giant fullerenes. Strain in the giant fullerenes is expected to be focused in the regions of the corannulene-like cusps. The surface thus becomes a smoothly curving network connecting the twelve cusps (reprinted from ref 108; copyright 1988 Macmillan Magazines Ltd.).

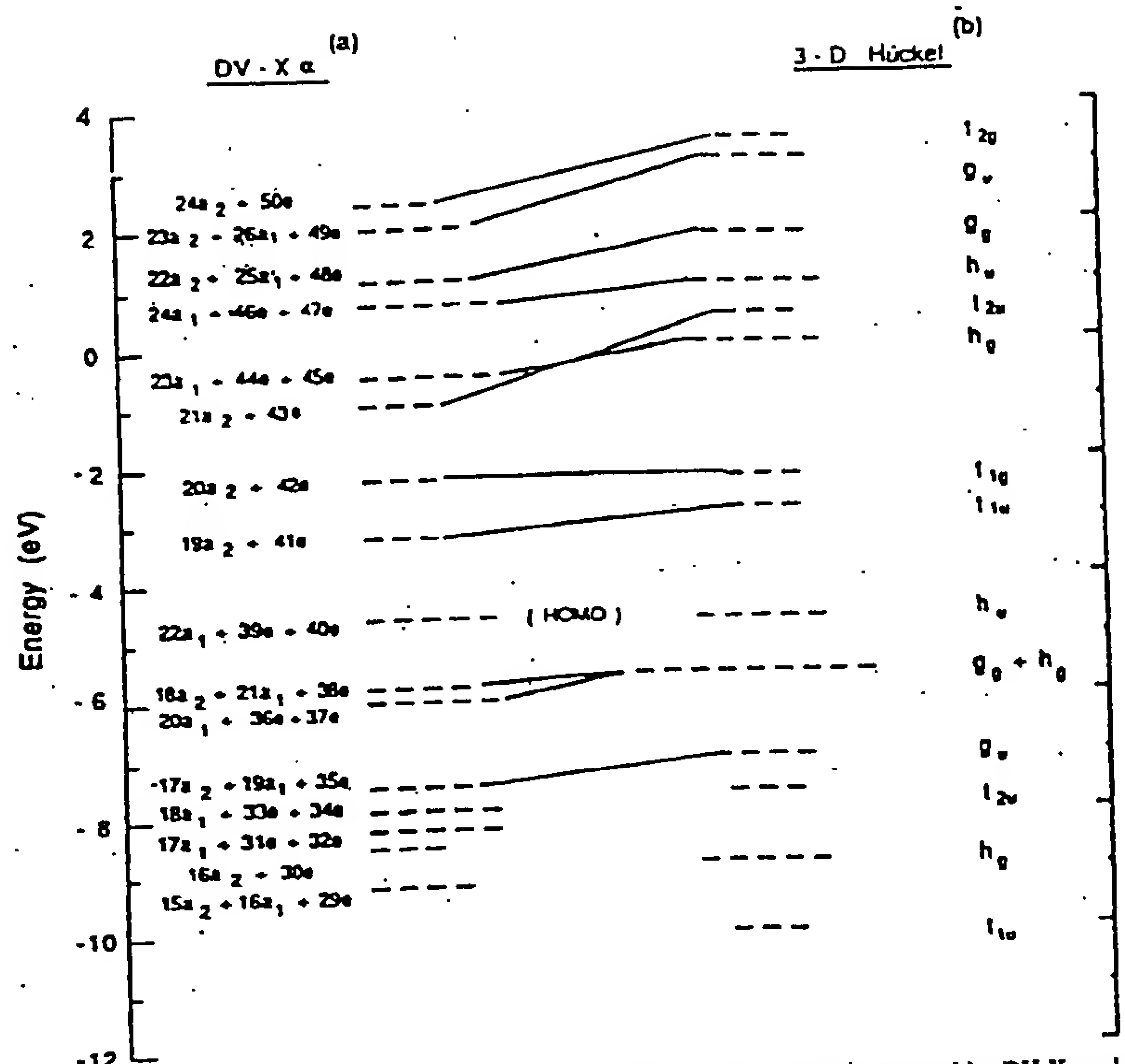

Figure 23. Orbital energy level diagram for fullerene-60 presented by Hale.[169] The energies derived by DV-Xα calculations assuming D_3 symmetry on the left are compared with Hückel results. In the diagram β has been given the value −2.52 eV (reprinted from ref 169; copyright 1986 American Chemical Society).

large-scale restricted Hartree-Fock calculations and they deduced that ΔH_f = 415–490 kcal/mol (relative to graphite) the electron affinity should be 0.8 eV and the ionization energy 7.92 eV. The electron affinity (2.4 eV) has been calculated by Larsson, Volosov, and Rosen[166] and by Braga et al.[167] Schulman and Disch[168] have calculated the heat of formation on the basis of ab initio SCF theory.

Hale[169] determined electronic properties, such as the ionization energy for fullerene-60, by the discrete variational (DV)-Xα method using the Slater transition state formalism. Such calculations tend to be good for spheroidal systems. Hale's orbital energy level diagram for fullerene-60 is reproduced in Figure 23. The linear combination of muffin-tin orbital method in its atomic sphere approximation (LMTO ASA) was applied by Satpathy.[170] Calculations in which the partial retention of differential overlap PRDDO approach was applied were carried out by Marynick and Estreicher.[171] Stone's tensor surface harmonic theory was used by Fowler and Woolrich.[148] The IMOA method (iterative maximum overlap approximation) was applied to a range of fullerenes by Kovacevič, Graovac, and Babič[172] to assess hybridization, structure and the amount of strain in these cages. Haddon[173] has discussed degree of pyramidalization considerations for fullerene-60 and other aromatic compounds.

Fabre and Rassat have reviewed the properties of known aromatic molecules which are essentially com-

In some of the calculations the electronic spectra of the fullerenes were the main focus. The calculations of Kataoka and Nakajima[175] and László and Udvardi[176] used the Pariser–Parr–Pople method (with CI) to determine spectra, structural parameters, and oscillator strengths. Optimized INDO calculations were published by Shibuya and Yoshitani.[177] The electronic structure and the spectra have also been studied by the CNDO/S method (including CI) by Larsson et al.[166] and by Braga et al.[167] Hayden and Mele[178] evaluated π-bonding behavior using the tight-binding model with electron–phonon coupling for the ground and excited states of fullerene-60. Jahn–Teller instabilities in the excited electronic states and the ion have been classified by Negri, Orlandi, and Zerbetto[179] who have also estimated Franck–Condon patterns and phosphorescence quantum yields.

Several calculations focused on the vibrational properties of fullerene-60. The result of primary (and historical) significance is that only four fundamentals are IR active due to the high symmetry of the molecule. Of the 174 vibrational modes giving rise to 42 fundamentals of various symmetries, four have t_{1u} symmetry and are IR active whereas 10 (eight h_g and two a_g) are Raman active.

Newton and Stanton[181] gave preliminary details of the vibrational behavior of fullerene-60 using MNDO theory. A non-Cartesian coordinate method was employed to describe the C_{60} vibrations in terms of four-force field constants by Wu, Jelski, and George.[180] Ab initio

SCF/STO-3G calculations of the vibrational properties of C_{60} and other symmetric carbon cages have been published by Disch and Schulman.[181] Schulman et al.[182] have applied the ab initio and AM1 methods to fullerene-24 and fullerene-60 in order to obtain heats of formation, vibrational frequencies, and ionization energies. Coulombeau and Rassat have considered the vibrations of several fullerenes up to fullerene-120.[183] They have also discussed hydrofullerenes.[184] In addition to calculating the rotational properties on the basis of icosahedral symmetry analysis,[184] Weeks and Harter have carried out a normal mode study on the basis of a classical spring/mass model.[185] They have also discussed the rovibrational properties of fullerene-60.[185-189] Stanton and Newton[190] extended and revised earlier MNDO studies giving detailed information on the normal modes. They have derived group theory invariance theorems for vibrational analysis and have discussed the A_u vibration which essentially consists of rotary oscillations of the pentagonal rings. Cyvin et al.[191] used a 5-parameter force field to calculate the frequencies of the four IR active and 10 Raman-active modes; and Brendsdal et al.[192] have considered approximate methods in order to determine all 46 vibrational frequencies. Brendsdal[193] has discussed the symmetry coordinates.

Slanina et al. have carried out a harmonic vibrational analysis within the AM1 method for fullerene-60 and also fullerene-70.[194] The study has been extended to include consideration of structural, energetic, and thermodynamic properties of both species using MMP2 and MNDO methods.[195-197] Bakowies and Thiel[198,199] have used the MNDO approach to calculate the IR spectra of a whole range of fullerenes from C_{24}–C_{240}. For C_{70} they deduce that one vibrational band should be significantly more intense than the rest, see section X.

Heymann has discussed the possibility that He may be trapped in a fullerene-60 cage.[200] Calculations have been made of the spectroscopic properties of various intracage complexes by Ballester et al.[201] assuming the central atom is trapped in a polarizable uniform (spherical) dielectric cage. Kroto and Jura[202] have discussed the importance of charge-transfer processes in the spectra of neutral and ionic fullerene intra- as well as extracage (van der Waals) complexes. For the ions the energy is just the difference between the ionization potentials of the C_{60} cage and the encapsulated species. Van der Waals complexes such as $C_{60}{\cdot}H^+$ are likely to be particularly important (section XI). Rosen and Waestberg have calculated the electronic structure of $C_{60}La$ (and C_{60}) obtaining ionization energies and electron affinities for the neutral and ionic species within the local-density approximation.[203,204] Saito[205] has also used the local density approximation to calculate the electronic properties of $C_{60}M$ (M = K, O, Cl).

Theoretical calculations have been carried out on fullerene-60 derivatives such as hydrofullerenes by Coulombeau and Rassat[184] and by Scuseria[206] who has also considered the perfluorofullerene, $C_{60}F_{60}$. Crystal packing considerations for spheroidal molecules including fullerene-60, have been discussed by Williams.[207]

Several papers have focused on the likely electrical and/or magnetic properties of the fullerenes in particular fullerene-60. Elser and Haddon,[208,209] using HMO and London theory, calculated the ring current magnetic susceptibility and concluded that the shielding should be vanishingly small (less than 1 ppm) due to cancellation of the diamagnetic and paramagnetic contributions. They concluded that fullerene-60 should not show normal aromatic behavior. Studies by Fowler, Lazzeretti, and Zanasi[210] and Pauling[211] have suggested however that the diamagnetic term has been underestimated. From large scale ab initio, coupled Hartree–Fock calculations (involving all electrons) of the polarizability and magnetizability of C_{60} and C_{20}^{2+}, Fowler et al.[210] conclude that the shielding should be roughly the same as for related aromatic systems. Haddon and Elser[212] have discussed their own results[208,209] and reinterpreted those of Fowler et al.[210] and conclude that the latter study is consistent with a small delocalized susceptibility. Schmalz[213] has argued that the Fowler et al.[210] interpretation is correct. The NMR study of Taylor et al.[6] yielded a chemical shift for fullerene-60 which is fairly typical for an aromatic species. Fowler et al.[214] have extended their approach to the calculation of the shifts in fullerene-70, obtaining results consistent with observation and confirming the line assignments made by Taylor et al.[6] This problem is further discussed in section X.

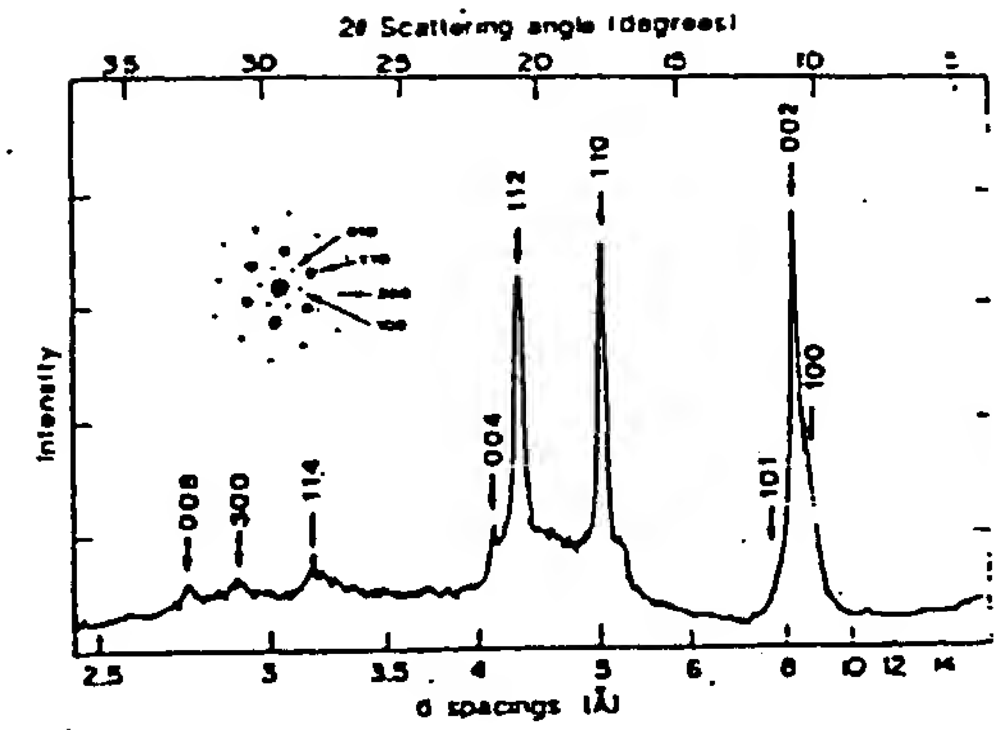

Figure 24. X-ray diffraction pattern of a microcrystalline powder of fullerene-60 obtained by Krätschmer, Lamb, Fostiropoulos, and Huffman.[4] Inset (upper left) is a single-crystal electron diffraction pattern (shown in more detail in Figure 25) indexed with Miller indices compatible with the X-ray pattern. This pattern provided unequivocal evidence that the C_{60} species they had isolated was a round ball 10 Å in diameter in perfect agreement with expectation for buckminsterfullerene (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

IX. The Isolation, Separation, and Structural Characterization of Fullerenes-60 and -70

Almost five years, to the day, since the special behavior of the C_{60} signal was recognized (Figure 5) and the buckminsterfullerene proposal made,[3] macroscopic samples were isolated and characterized. Krätschmer, Lamb, Fostiropoulos, and Huffman,[4] in following up their earlier IR observations,[5,74] discovered that at ca. 300–400 °C a solid material could be sublimed from the deposit obtained from arc-processed graphite. They found that this sublimate was soluble in benzene and could be crystallized. The X-ray and electron diffraction analyses (Figures 24 and 25) of the crystalline material so obtained (Figure 26) showed it consisted of arrays of 7 Å diameter spheroidal molecules separated

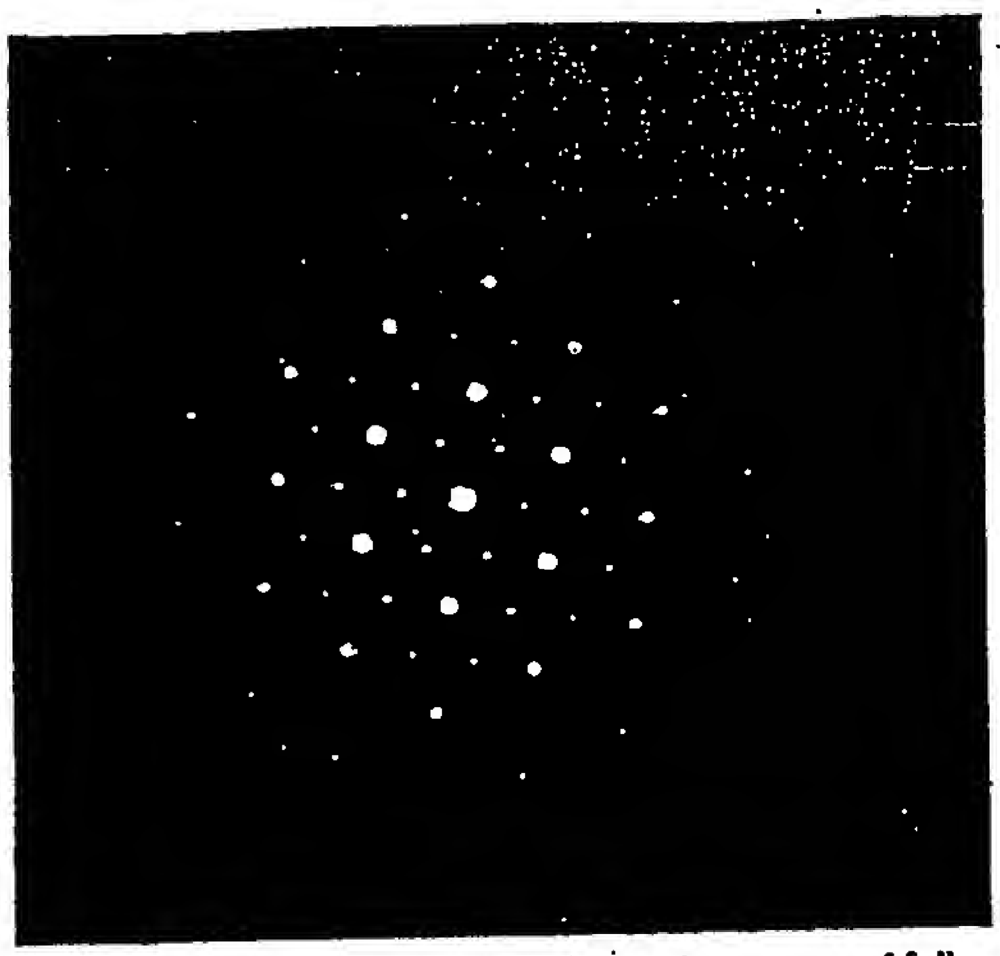

Figure 25. Single-crystal electron diffraction pattern of fullerene-60.[4] Further details of indices are given in Figure 24 (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

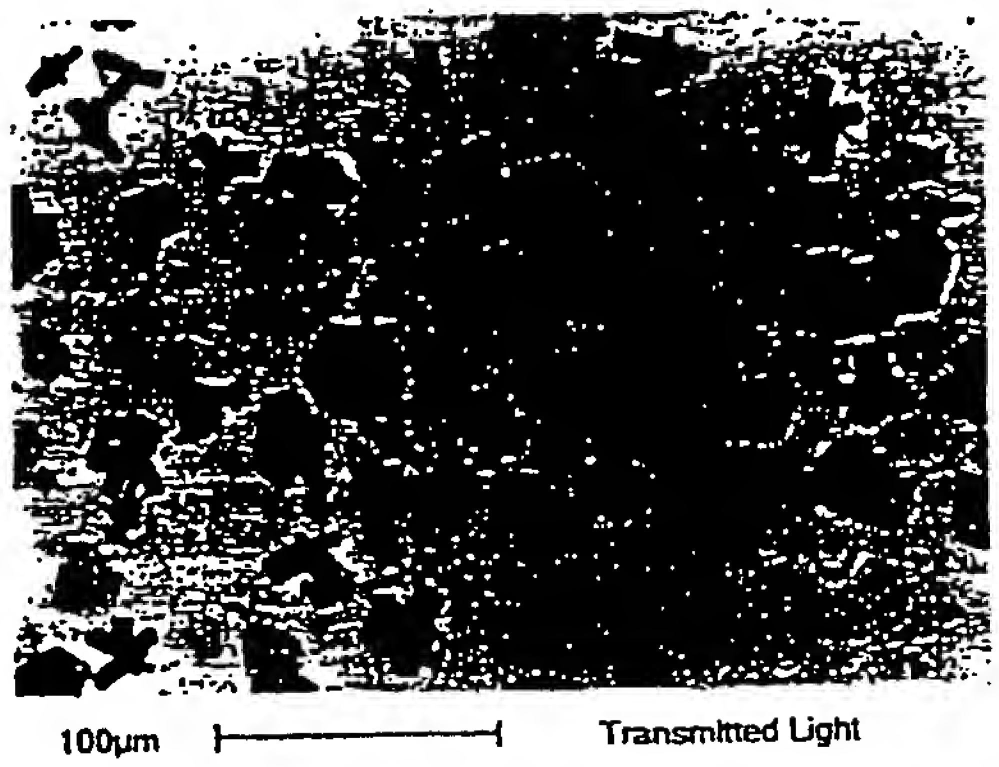

Figure 26. Transmission micrograph of crystals extracted by Krätschmer et al.[4] from the deposit of arc-processed graphite. Thin platelets, rods and stars of hexagonal symmetry are observed (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

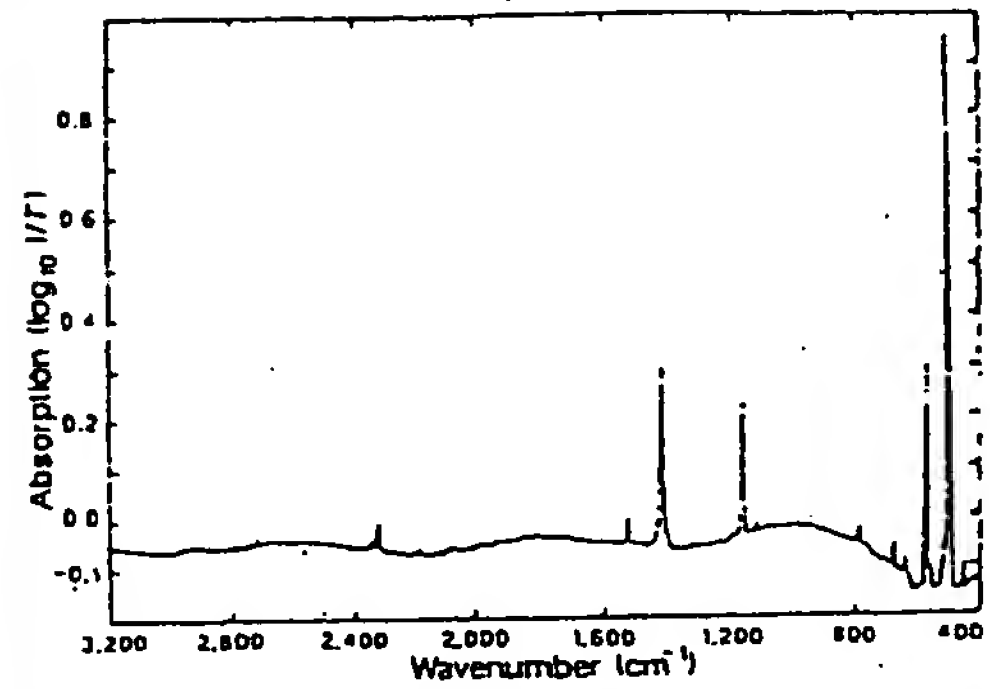

Figure 27. Infrared spectrum of fullerene-60 presented by Krätschmer et al.[4] showing the four fundamentals in excellent agreement with expectation for the proposed fullerene-60 structure. Weaker features belong to fullerene-70 (reprinted from ref 4; copyright 1990 Macmillan Magazines Ltd.).

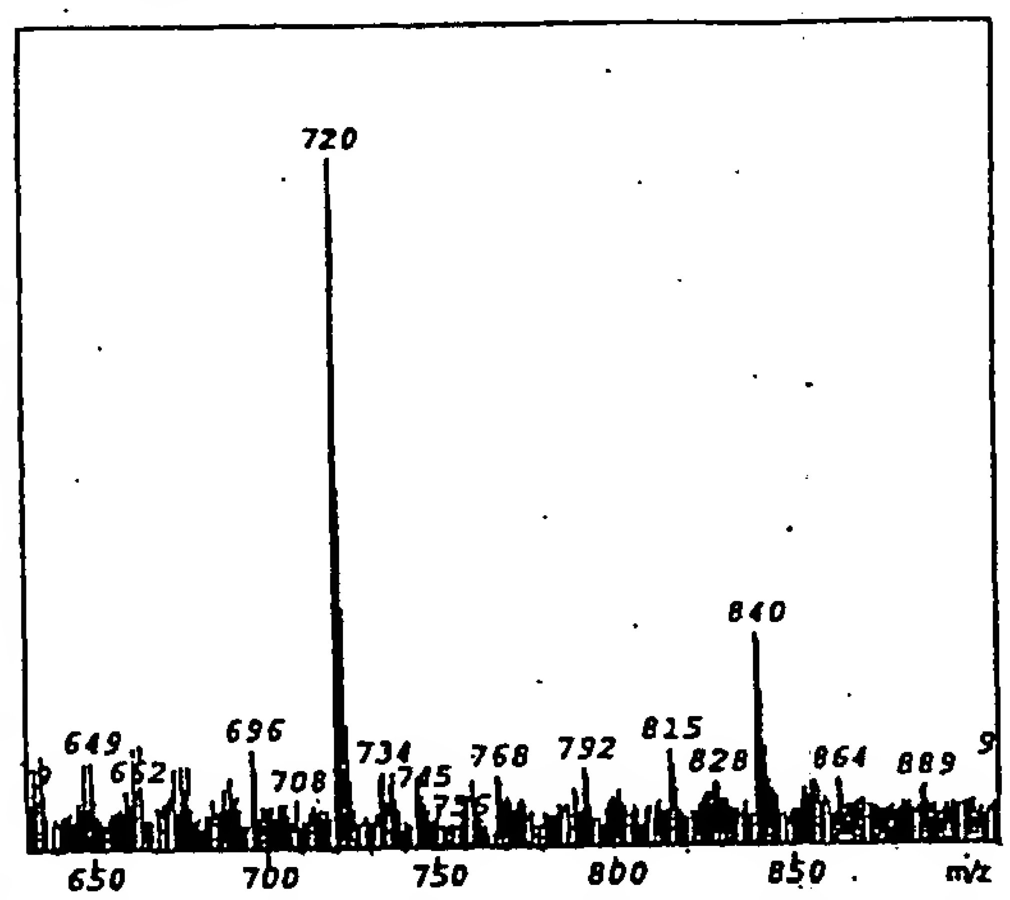

Figure 28. FAB-sampled mass spectrum, obtained by Taylor et al.,[6] of the soluble material extracted from arc-processed graphite. Apart from unequivocal evidence for C_{60} and C_{70} in the extract there is also evidence for other even-numbered carbon species, particularly C_{58} and C_{68} (reprinted from ref 6; copyright 1990 The Royal Society of Chemistry).

by ca. 3.1 Å (in graphite the interlayer distance is 3.4–3.5 Å). These authors also reported IR (Figure 27), UV/vis, and mass spectra of the extracted material. Bands of C_{70} were present (weakly) in the IR spectrum and, in the UV/vis spectrum, some features of fullerene-60 were masked by those of fullerene-70. These results provided the first confirmation of the fullerene-60 structural proposal.

In a parallel and independent study of similarly arc-processed carbon, Taylor et al.[6] had also shown that C_{60} was present by FAB-sampled mass spectrometry and that a red soluble extract could be obtained by treating the carbon deposit directly with benzene. Taylor et al.[6] processed the extract by the Soxhlet procedure and obtained a material which mass spectrometry showed to contain a range of fullerenes, C_{60} and C_{70} in particular (Figure 28). This material was chromatographed by using hexane/alumina, and C_{60} and C_{70} were thereby separated into a magenta and red fractions, respectively. ^{13}C NMR measurements yielded a single line for C_{60} (Figure 29a) providing definitive proof that all 60 atoms are equivalent—a result totally commensurate with the buckminsterfullerene structure. There is of course the alternative solution that all the atoms are located on the perimeter of a monocyclic ring. This (explosively) unlikely possibility was eliminated by the NMR spectrum of C_{70} which consisted of a set of five lines (Figure 29c) with a chemical shift pattern and relative intensities commensurate with the fullerene-70 structure (Figure 30b) first suggested by Heath et al.[7] This result not only confirmed the fullerene 5/6-ring geodesic topology but also eliminated the possibility that the carbon atoms might be fluxional. Almost as important is the confirmation, by this result, of the existence of other members of the fullerene family.

X. Postbuckminsterfullerene Research—The First Results

Since the revelation that macroscopic samples of the fullerenes can be isolated and that they are soluble and

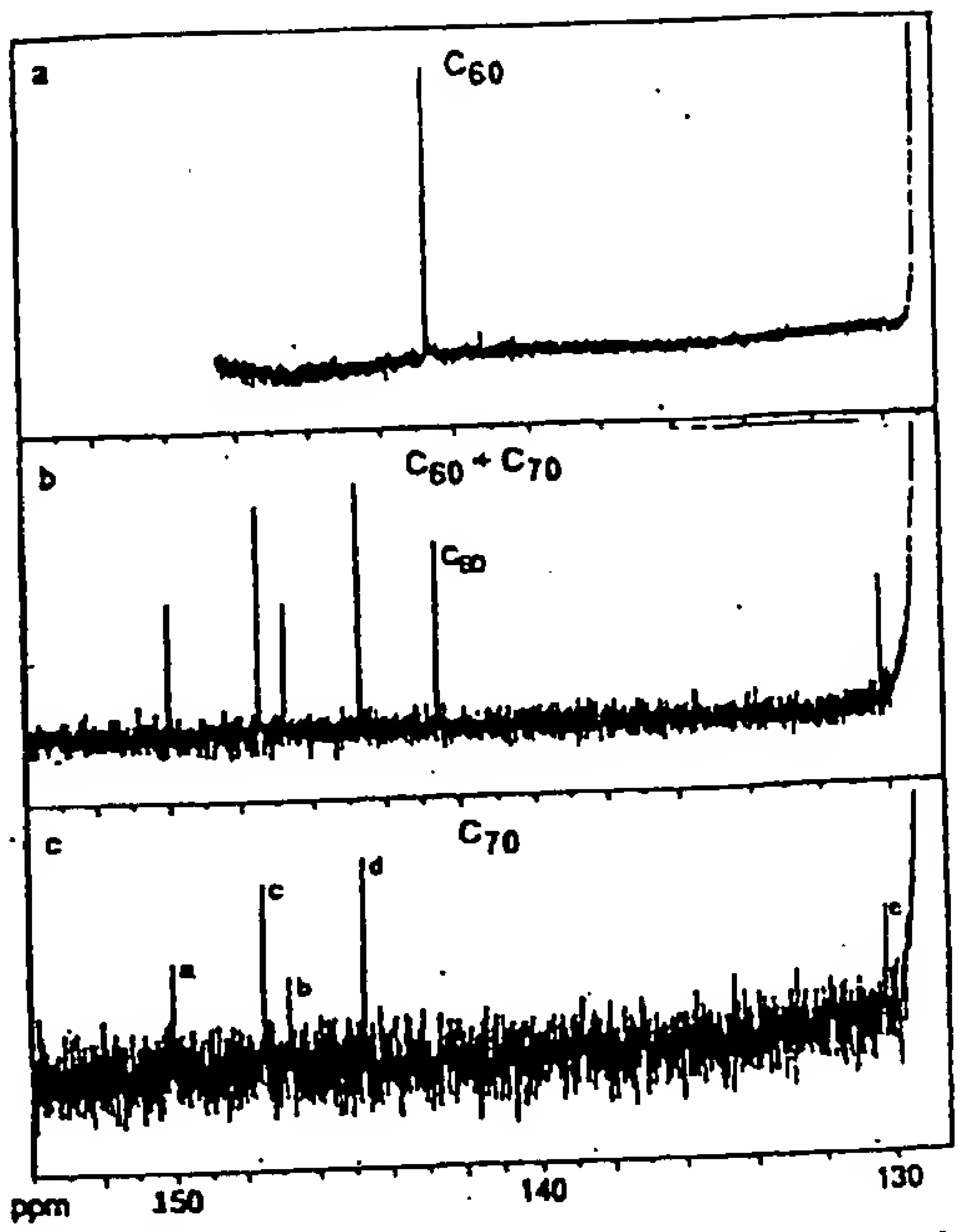

Figure 29. ^{13}C NMR spectra obtained from chromatographically purified samples (Taylor et al.[6]) of soluble material extracted from arc-processed graphite: (a) ^{13}C NMR spectrum of a purified sample exhibiting only a single resonance, (b) spectrum of a mixed sample, and (c) spectrum of a purified sample of C_{70} from which C_{60} has been eliminated. These spectra are consistent with the structures and assignments presented in Figure 20. The wing of the intense benzene solvent signal lies to the far right-hand side. This set of observations provided unequivocal evidence that the carbon atoms in C_{60} were indeed all equivalent in perfect agreement with expectation if the molecule were buckminsterfullerene (Figure 30). The five-line spectrum for C_{70} is also totally consistent with that expected for (D_{5h})fullerene-70 (Figure 30).[7] This spectrum eliminated any lingering doubt there might have been that the C atoms were either fluxional or perhaps located on the perimeter of a monocyclic ring. It also provided evidence for the stability of other members of fullerene family[7-9] (reprinted from ref 6; copyright 1990 The Royal Society of Chemistry).

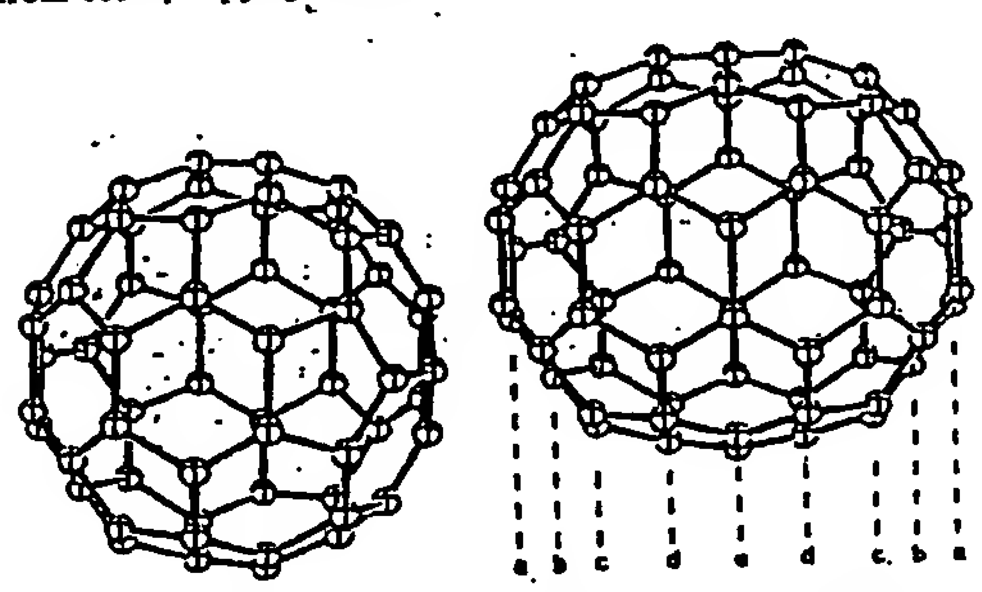

Figure 30. Schematic diagrams of fullerene-60 and fullerene-70 (based on diagrams of Slanina et al.[194]). All sixty atoms in fullerene-60 are equivalent whereas fullerene-70 possesses five different types of carbon in the ratios 10:10:20:20:10 in the order abcde respectively as shown. Compare with the NMR spectrum shown in Figure 29.

chromatographically separable, it is now the turn of experimentalist to have a ball. Ajie et al.[215] and Hare et al.[216] have observed the UV/visible spectra of chro-

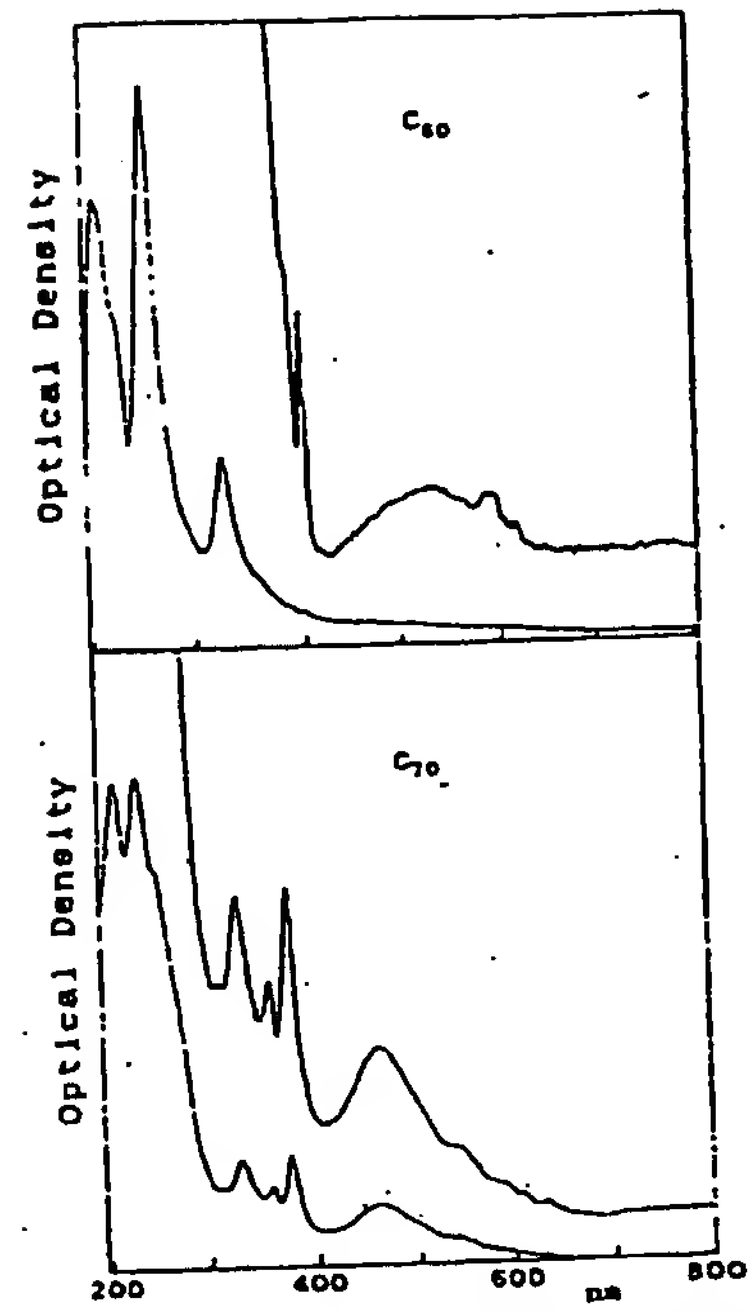

Figure 31. UV/vis spectra of chromatographically separated fullerene-60 and fullerene-70[216] in hexane solution (reprinted from ref 216; copyright 1991 Elsevier Science Publishers).

TABLE I. Properties of C_{60} Buckminsterfullerene

Vibrational Frequencies		
abs(obs)[a]	em(obs)[b]	calc, cm^{-1} [c]
528	527.1	472
577	570.3	618
1183	1169.1	1119
1429	1406.9	1434

X-ray Data[d,e]

r(C–C) = 1.388 (9) Å six–six ring fusion
r(C–C) = 1.432 (5) Å five–six ring fusion

NMR Data[f,g]

chemical shift (benzene soln) 142.68 ppm

Electronic/Spectroscopic Data

electron affinity[h]	2.6–2.8 eV
ionization energy[i]	7.61 (0.02) eV
UV/vis bands[j,k]	213, 257, 329 (ϵ_{max} = 135 000, 175 000, 51 000) 404 (w) 440–670 (brd) (max. 500, 540, 570, 600, 625) nm

[a] Reference 4. [b] Reference 218. [c] Reference 191. [d] Reference 222. [e] See also Figures 24, 32, and 34. [f] See Figure 28. [g] Reference 6 (see also refs 215 and 228). [h] Reference 99. [i] References 101, 102, 239, and 240. [j] Reference 216 (see also ref 215). [k] See also Figure 31.

31). Reber et al.[217] have observed a luminescence spectrum. Frum et al.[218] have observed a most interesting IR emission spectrum from a hot gas-phase fullerene sample. The frequencies of the observed bands are given in Table I.

The availability of significant quantities of fullerenes has also opened up a Round Postbuckminsterfullerene Era of polycyclic aromatic chemistry. Haufler et al.[219] found that C_{60} can undergo Birch reduction to produce a white solid of formula $C_{60}H_{36}$. They point out that this formula is consistent with a cage hydrocarbon in

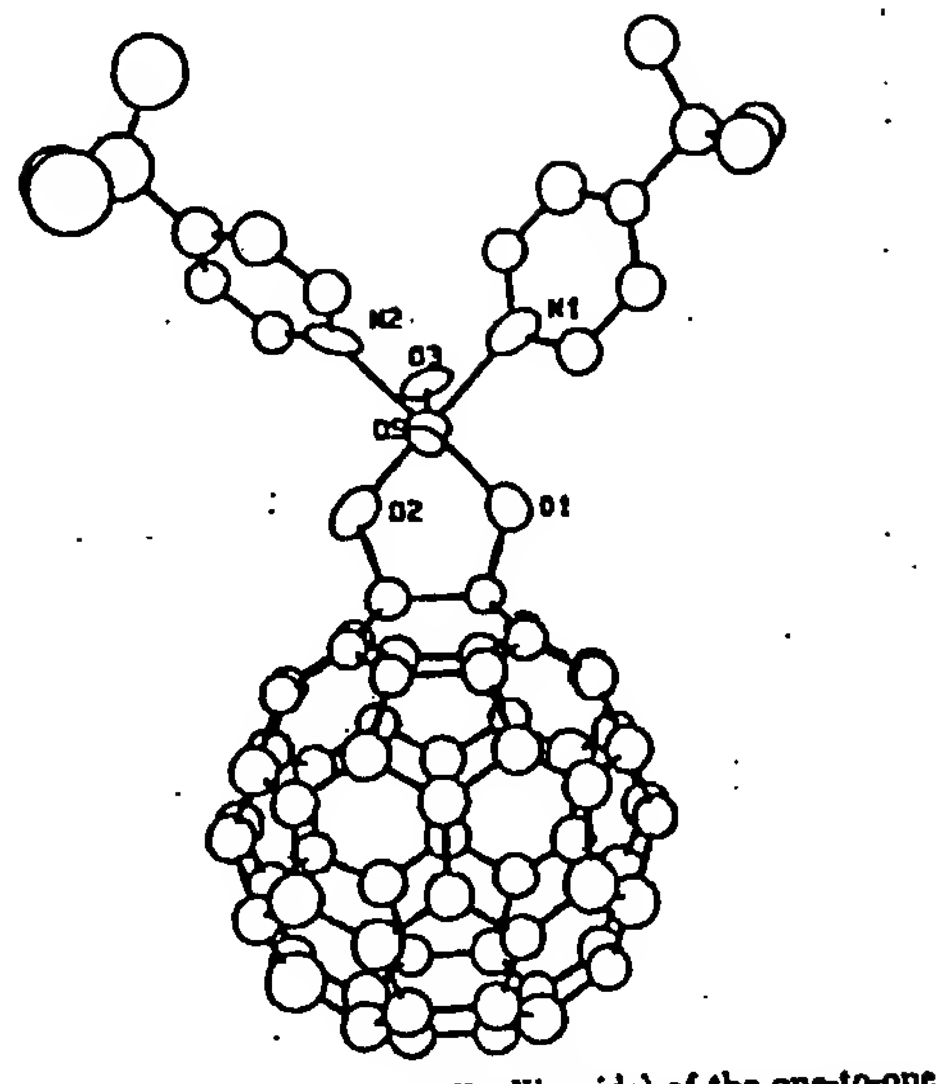

Figure 32. ORTEP drawing (50% ellipsoids) of the one-to-one C_{60}-osmium tetroxide adduct $C_{60}(OsO_4)$(4-*tert*-butylpyridine)$_2$ showing the relationship of the osmyl unit with the fullerene-60 carbon network[222] (reprinted from ref 222; copyright 1991 the American Association for the Advancement of Science).

which 12 isolated double bonds remain, possibly in the pentagonal rings. The reduction appears to be reversible. Evidence for the existence of a $C_{60}U$ complex was obtained by the laser vaporization approach, used originally to detect $C_{60}La$.[7] These authors also described the results of cyclic voltammetry measurements which indicated that C_{60} has two reduction potentials. Similar measurements have been made by Allemand et al.[220] who obtained a third potential. Their cyclic voltammetry measurements indicate that, curiously, fullerenes-60 and -70 appear to exhibit similar electrochemical behavior.

In one of the first attempts to introduce functional groups, Hawkins et al.[221] have found that they can form adducts of fullerene-60 with OsO_4(4-*tert*-butylpyridine) and its analogues. In a further study Hawkins et al.[222] have now obtained crystals of the osmium complex shown in Figure 32 and shown by X-ray analysis that rotation of the free C_{60} spheroids in the solid phase has been eliminated by the attached group. This study has yielded the first carbon-carbon bond lengths for the fullerene cage (Table I). Arbogast et al.[223] have observed fascinating photophysical behavior: fullerene-60 shows no fluorescence and efficiently catalyzes the formation of singlet oxygen. These authors observe a small S-T splitting of ca. 9 kcal/mol which is probably due to the large diameter of the molecule and the resulting small electron-electron repulsion energy. This together with the very low fluorescence rate and probably large spin-orbit interaction appears to account for the fact that intersystem crossing is a dominant process. Attention has been drawn to the fact that, due to their photophysical activity, care should be taken when working with fullerenes.

Hare et al.[224] and Bethune et al.[225] have made infrared measurements on chromatographically separated sam-

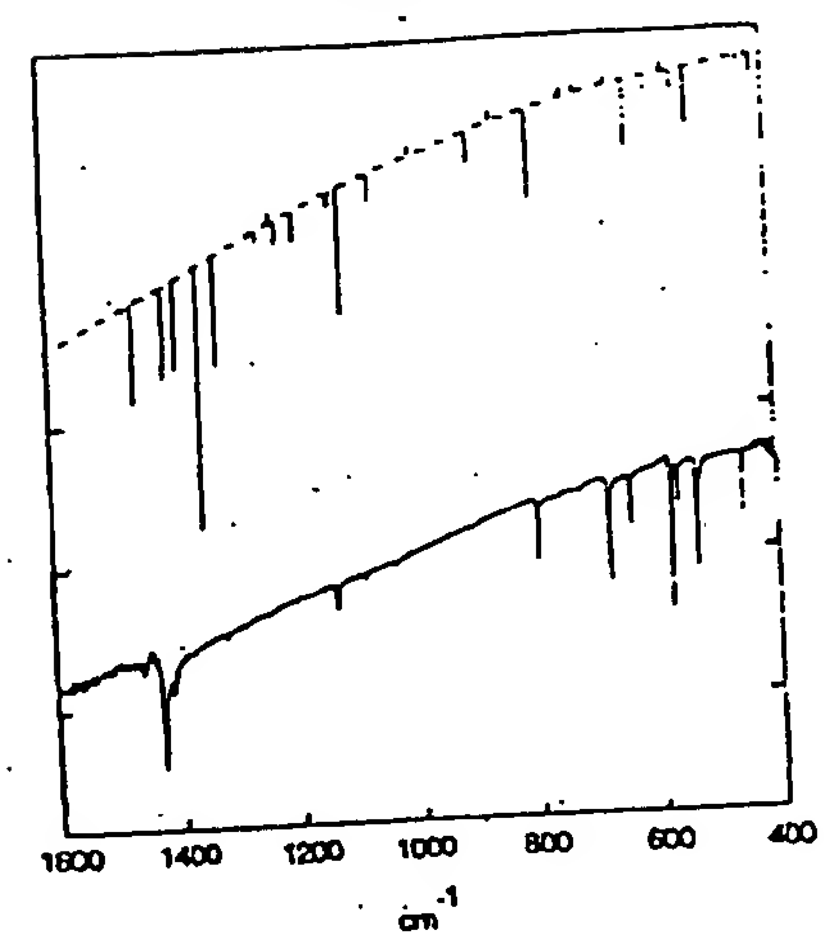

Figure 33. Infrared spectrum of chromatographically purified fullerene-70 obtained by Hare et al.[224] and compared with the calculated spectrum of Bakowies and Thiel.[198,199] The dashed curve is an estimated baseline. Note that the intensity of the very strong band calculated to lie near 1400 cm^{-1} has been arbitrarily reduced by a factor of 3 relative to other features. Features calculated to be very weak are indicated by markers *above* the estimated baseline (reprinted from ref 224; copyright 1991 The Royal Society of Chemistry).

ene-70 together with the calculated spectrum of Bakowies and Thiel[198,199] is presented in Figure 33. Bethune et al.[226] and Dennis et al.[227] have also made Raman measurements of fullerene-60 and -70. Liquid-phase NMR studies of unpurified fullerene mixtures by Johnson et al.[228] confirmed the result of Taylor et al.[6] (carried out on fully chromatographically purified samples) that the fullerene-60 resonance is a single line. Ajie et al.[215] have also confirmed the NMR measurements of a single line for fullerene-60 and five lines for fullerene-70; the former on a separated sample, the latter on a mixed fullerene-60/-70 sample. A 2D NMR analysis on fullerene-70 by Johnson et al.[229] has unequivocally confirmed the assignments made previously by Taylor et al.[6] shown in Figures 29c and 30b. Further refinements by Fowler et al.[214] of previous studies[210] predict fullerene-60 chemical shifts in excellent agreement with experiment (within 3 ppm). The study also includes estimates of the shifts for fullerene-70 so supporting further the pattern of line assignments given by Taylor et al.[6] (Figures 29c and 30b). Tycko et al.[230] and Yannoni et al.[231] have made solid-state NMR measurements down to 177 K where the motion is sufficiently slow for chemical shift tensor data to be obtained. Fullerene-60 rotates isotropically at 296 K and fullerene-70 rotates somewhat more anisotropically. Haddon et al.[232] have measured the magnetic susceptibility of solid samples of fullerenes and found it consistent with a molecule with a small ring current (see discussion in section VIII). Fowler[233] notes that when this result is compared and contrasted with the NMR shift of fullerene-60[6] it may imply ambivalent character when the question of the molecules "aromaticity" is considered.

Perhaps scanning tunneling microscopy (STM) offers more than any other a satisfying feeling of what the

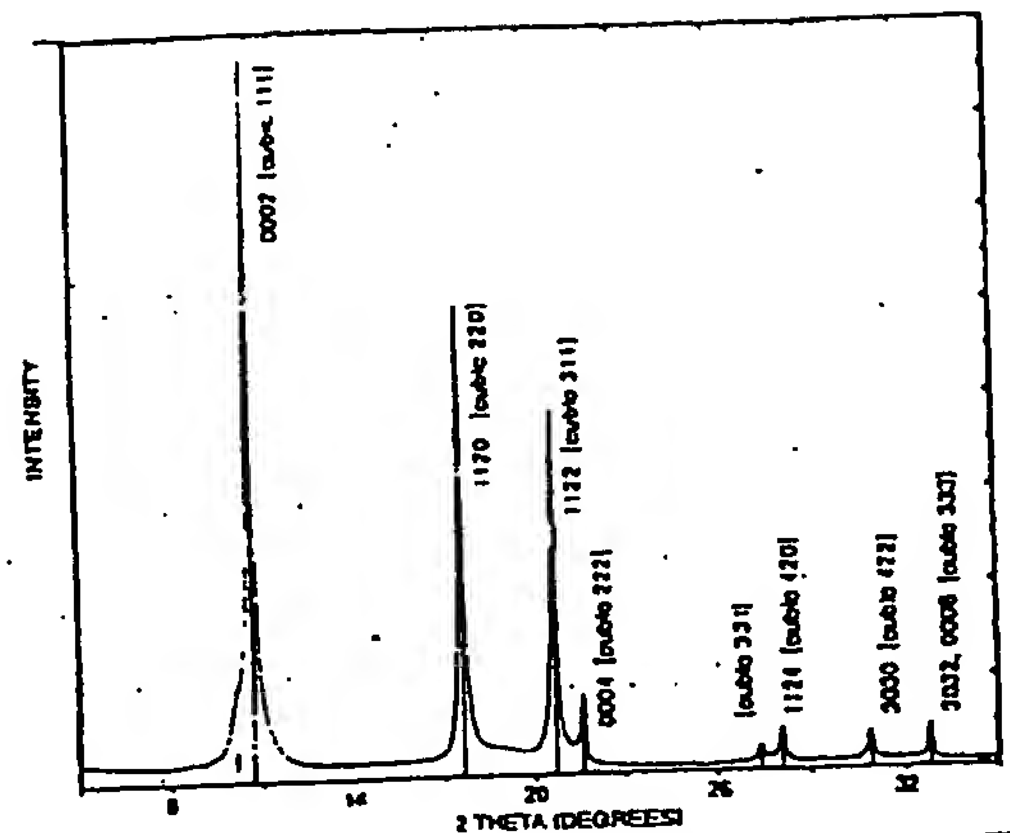

Figure 34. X-ray diffraction pattern obtained by MacKay et al.[237] from a chromatographically purified fullerene-60 sample. The structure revealed is basically that of a strongly disordered stacking of a simple hexagonal close-packing, exactly as for elemental cobalt. The hexagonal unit cell refines to $a = 10.017 \pm 0.004$ Å and $c = 16.402 \pm 0.01$ and contains two C_{60} spheres. The spheres would be 10.017 Å between centers and the calculated density would be 1.68 g cm^{-3}. The lines can be indexed as shown and it will be noted that, because of the stacking disorder, only those reciprocal lattice rows parallel to c for which $-h + k = 3n$ are present. The c/a ratio of 1.637 is very close to the theoretical value of 1.633 and thus the pattern can also be indexed with respect to a face-centered cubic lattice (with $a = 14.186$ Å) (as of copper metal) with stacking disorder which removes the 200 and 400 reflections and which introduces a very weak line (the first) at a spacing of $a/(8/3)^{1/2}$ due to double diffraction from stacking faults. The intensity variation of the pattern as a whole corresponds to the transform of a sphere of radius 3.5 Å giving a first minimum in the region of $2\theta = 25°$. Since the crystal is a mixture of FCC and HCP arrays, extracted crystalline material probably contains solvent molecules trapped in the faults.

et al.,[235] and Chen et al.[236] have deposited fullerene monolayers on gold and studied them by STM. The spherical molecules tend to form mobile hexagonally packed arrays on a surface. Chen et al.[236] observed local density variations on the surface of fullerene-60 which are highly suggestive of five- and six-membered rings.

The preliminary X-ray observations were made by Krätschmer et al.[4] working with crystalline material consisting mainly of fullerene-60 with some fullerene-70 present. A recent X-ray diffraction image was obtained by MacKay et al.[237] using chromatographically purified fullerene-60 (Figure 34). This image is commensurate with a completely random mix of HCP and FCC arrays of fullerene-60 molecules. Fleming et al.[238] obtained purely FCC structured crystals from vacuum sublimed material. The implication is that interstitially trapped solvent probably stabilizes the mixed FCC/HCP crystals. It appears that fullerene-60 spheres are rotating in the lattice[231] and that when rotation ceases at low temperature the crystals are still disordered at the atomic level.[221,222,238]

A most interesting study as far as theoretical chemistry is concerned is that of Lichtenberger et al.[239,240] who measured the photoelectron spectrum of fullerene-60 on a surface and in the gas phase (Figure 35). The results are in good agreement with the theoretical (DV)-Xα study of Hale[169] (Figure 23). The first IP of fullerene-60, 7.61 eV, is nicely consistent with the result obtained by Zimmerman et al.[101] and McElvany.[102]

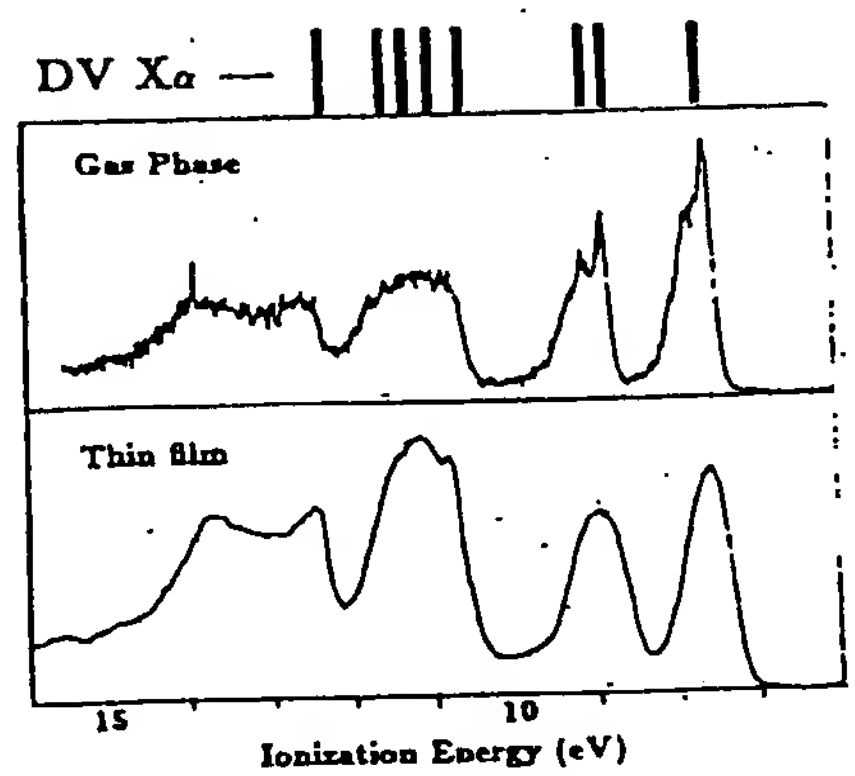

Figure 35. Gas phase (upper) and thin film (lower) He I valence photoelectron spectra of fullerene-60 obtained by Lichtenberger et al.[239,240] The DV-Xα results of Hale[169] (see Figure 23) which appear to be in good agreement with observation are indicated (reprinted from ref 239; copyright 1991 Elsevier Science Publishers).

Luffer and Schram[241] have made electron ionization mass spectrometric measurements on fullerene-60.

Several papers presented at a special symposium on the fullerenes (Nov 1990) have been collected together and published by Averback et al.[242] Some of the most important experimentally determined properties of fullerenes are presented in the Table I.

XI. Astrophysical Implications of C_{60}

Although low-temperature ion-molecule processes (Herbst and Klemperer[243] and Dalgarno and Black[244]) can account for most interstellar species, the long cyanopolyynes presented a problem. It was experiments which probed the possibility that carbon stars might be responsible for them[31,32] which revealed the stability of fullerene-60.[3] An important aspect of the experiments lay in the possibility of probing the conjecture of Douglas[40] that carbon chains might be responsible for the diffuse interstellar bands (DIBs). The DIBs are a set of interstellar optical absorption features of varying widths which have puzzled astronomers and spectroscopists since the mid-1930s. Herbig has published the definitive analysis of these features.[245,246] Many possible contenders for the carrier have been suggested, however no generally accepted explanation exists so far. This is strange as the species responsible is clearly abundant, chemically bound (i.e. not atomic), and must be quite stable in order to survive in the hostile interstellar environment or, if destroyed, be very efficiently reformed. The types of carrier appear to be few in number and must have very large electronic absorption coefficients.

The possibility that C_{60} might be the widely distributed in the Universe and particularly in the outflows from carbon stars was suggested when the original discovery of its stability was made.[3] It was also pointed out that the fullerene-60 surface might be an important site for the catalysis of interstellar reactions and perhaps it (*or a derivative*) might be responsible for such features as the DIBs. There is one key argument,[50,55-68] associated with the proposal that fullerene analogues (ionized or un-ionized, complexed or otherwise) may be

the carriers has that all previous suggestions do not: fullerene-60 and its analogues are unique in that they appear to survive the violent processes which occur when the atomic components of a chaotic plasma condense to form particles. Various aspects of this original conjecture, particularly with regard to possible derivatives such as intracage complexes both ionized and neutral, have been discussed[55-58] in general terms.

As far as the neutral fullerene-60 species in space is concerned, the negative results of searches based on the laboratory measurement[98] has been published by Snow and Seab[247] and Sommerville and Bellis.[248]

The conditions in the ISM are such that a large fraction of any fullerene-60 molecules present is likely to be ionized and thus it has been pointed out that the spectra of ionized fullerenes such as C_{60}^+ or fullerene analogues (such as the cage complexes $C_{60}M^+$) might be responsible for some astrophysical features.[55,57] Léger et al.[249] and Joblin et al.[250] have taken up the C_{60}^+ proposal and considered it further.

Complexed species (section VIII) in the interstellar medium are particularly interesting as any C_{60} present is likely to be ionized and probably have something stuck to its surface. As the DIBs exhibit features reminiscent of matrix spectra, the possibility that intracage complexes[55,57,201-203] as well as the extracage complexes[202] might be responsible has been discussed. Heymann[200] has considered the He intracage complexes and Ballester et al. other likely species containing O, Na, etc.[201] Kroto and Jura[202] draw particular attention to the fact that the charge transfer bands of the $(C_{60}M)^+$ intracage complex and the van der Waals extracage complex $(C_{60})^+$·M (M = alkali, alkaline earth, or other element) are likely to be very strong. Particularly interesting are possible relationships that charge-transfer transitions might have with the DIBs and perhaps also the strong unassigned 2170 Å absorption feature which has puzzled astronomers for over seven decades. Hoyle and Wickramasinghe[251] suggested that C_{60} itself might explain this feature and further calculations relating to this possibility have been discussed by Braga et al.[167] Rabilizirov[252] has also discussed these possibilities. Wright[253] has discussed the general optical/UV characteristics of fullerenes and concludes that the observed interstellar extinction is not consistent with the presence of significant quantities of spheroidal particles with graphite-like outer shells. In this respect the existence of the amorphous carbon surface layers surrounding the graphite cores of carbon microparticles may well be important.[116] From the UV/vis spectra obtained so far[4,215,216] it is clear that neutral fullerene-60 is not responsible for either the DIBs or the 2170 Å hump.

There are also some intriguing interstellar emission features in the IR, termed the unidentified infrared bands (UIBs), which have been assigned to PAH-like material by Duley and Williams,[254] Léger and Puget,[255] and Allamandola et al.[256] The assignment rests largely on the reasonable correspondence between the astrophysical frequencies and those of polycyclic aromatic molecules which are usually used for fingerprint identification of large PAHs. Balm and Kroto[257] have discussed the fact that, if the fullerene-60 concept is correct, PAH material in space is likely to be nonplanar. They point out that one feature, namely that at 11.3

The new results also offer possible new avenues of study as far as condensed carbonaceous matter in the cosmos is concerned. According to McKay et al.[258], caged carbon clusters may offer a plausible explanation of some of the isotope anomalies observed in the elemental analysis of carbonaceous chondrites particularly the ^{22}Ne anomaly. Clayton[259] has pointed out that condensation in the atmospheres of supernovae might explain the so-called Ne-E anomaly. McKay et al.[258] have suggested that this observation might be explained by encapsulation of ^{22}Na in fullerene cages or icospiral embryos during the dust formation phases that follow supernova and nova outbursts. Subsequently, the decay of ^{22}Na yields an encapsulated ^{22}Ne atom. Zinner et al.[260] have pointed out that isotope anomalies are only to be found in spheroidal carbon grains. So far the only evidence that C_{60} might exist in space is an unconfirmed report by Anderson.[261]

XII. Conclusions

It took some 15 or so years before the imaginative theoretical conjectures of Osawa and Yoshida[13,14] and Bochvar and Gal'pern[17,18] were realized in the discovery of the stability of the C_{60} mass spectrometric signal[3] in 1985. A further period of five years elapsed during which time many experimental measurements and theoretical studies were made. By-and-large the theoretical work (section VIII) substantiated the idea that buckminsterfullerene should be stable. As time elapsed the weight of circumstantial evidence grew and ultimately became convincing. The key observations include:

(1) Detection of monometallic complexes indicated that atom encapsulation was feasible.[7,96]

(2) Further cluster beam studies showed 60 to be a magic number whether the carbon species was positively or negatively charged or neutral.[64,66,52]

(3) Reactivity studies showed the molecule to possess an inertness that was consistent with closure and the absence of dangling bonds.[103,96]

(4) The pentagon isolation principle explained the observation of C_{60} as the first magic number and C_{70} as the *second*.[8,9] Thus it was shown that the fullerene hypothesis rested on the observation of two magic numbers and not just one. Further refinement of the geodesic principle explained other observed magic numbers.[8,9]

(5) Large fullerene networks were found to possess quasiicosahedral structures and thus related giant concentric cage species[108] appeared to explain the infrastructure of the carbon microparticles observed by Iijima.[109,110]

(6) Photoelectron measurements of Yang et al.[99] were also quite consistent with the fullerene conjecture.

These and other studies (discussed in sections V–VII) thus had laid the background against which the critical infrared observation of Krätschmer et al.[5,74] was made. They were led to make this observation by considering that some intriguing optical features observed in 1982 might be due to buckminsterfullerene. These observations were followed up by Krätschmer, Lamb, Fostiropoulos, and Huffman[4] and Taylor et al.,[6] and the results have revolutionized the field in that now the material can be made in quantity and the properties of

It is interesting to note that the motives for the experiments which serendipitously revealed the spontaneous creation and remarkable stability[3] of C_{60} were astrophysical. Behind this goal lay a quest for an understanding of the curiously pivotal role that carbon plays in the origin of stars, planets, and biospheres. Behind the recent breakthrough of Krätschmer et al. in producing macroscopic amounts of fullerene-60, lay similar astrophysical ideas.[4] It is fascinating to now ponder over whether buckminsterfullerene is distributed throughout space, and we have not recognized it, and that it may have been under our noses on earth, or at least played an important role in some very common environmental processes, since time immemorial.

The material is already exhibiting novel physical and chemical properties and there can be little doubt that an exciting field of chemistry and materials science, with many exciting applications has opened up. One of its most important properties is its ability to accept electrons. The low-lying LUMO causes it to be a soft electrophile.

It is perhaps worthwhile noting that C_{60} might have been detected in a sooting flame decades ago and that our present enlightenment has been long delayed. How serious this delay has been only time will tell; however, already fullerene chemistry is a vibrant field of study and the prospects for new materials with novel properties is most promising. Certainly, a New Round Postbuckminsterfullerene World of carbon chemistry appears to have been discovered, almost overnight. It should not be long before the molecule becomes a standard in textbooks; indeed construction procedures for fullerene-60 and giant fullerenes are to be found in the educational literature.[126,262]

Warning

The UCLA group has pointed out the importance of treating the material with great caution at this time when so little is known about it.[263] Its ability to catalyze the formation of singlet oxygen and its novel chemical behavior inevitably suggest the possibility that the fullerenes might be carcinogenic. Particular care should be taken to ensure that the dust is not inhaled during preparation of the soot itself.

Acknowledgments. We are very happy to acknowledge the help of David Walton and Roger Taylor for helping to eliminate several obscurities from this article. We also thank Patrick Fowler for his help. Thanks are also due to all those who kindly sent reprints and we are grateful for permission to publish the data from several groups. S.P.B. thanks the SERC and AWA the Syrian Atomic Energy Commission for financial support.

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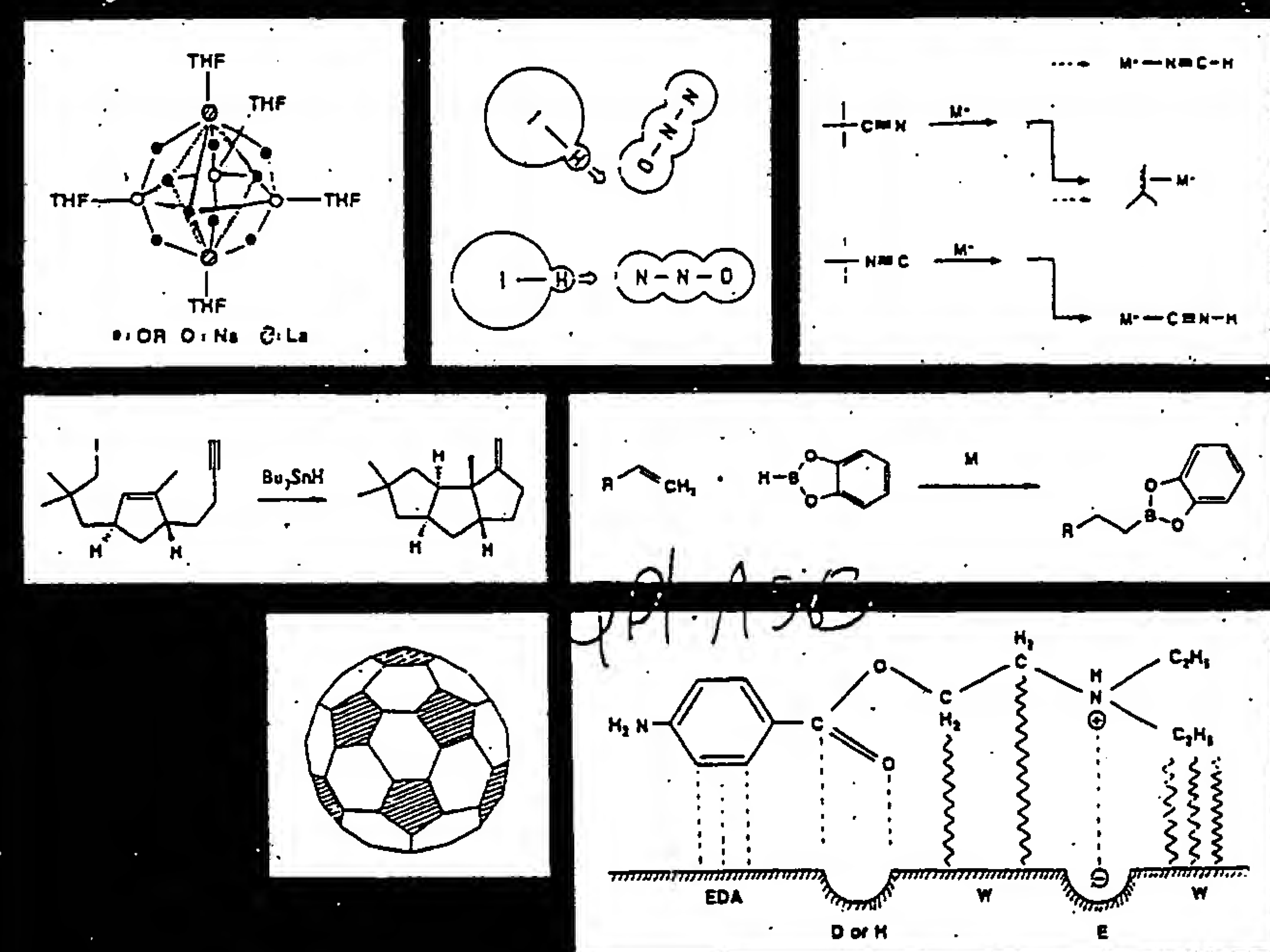
CHEMICAL REVIEWS



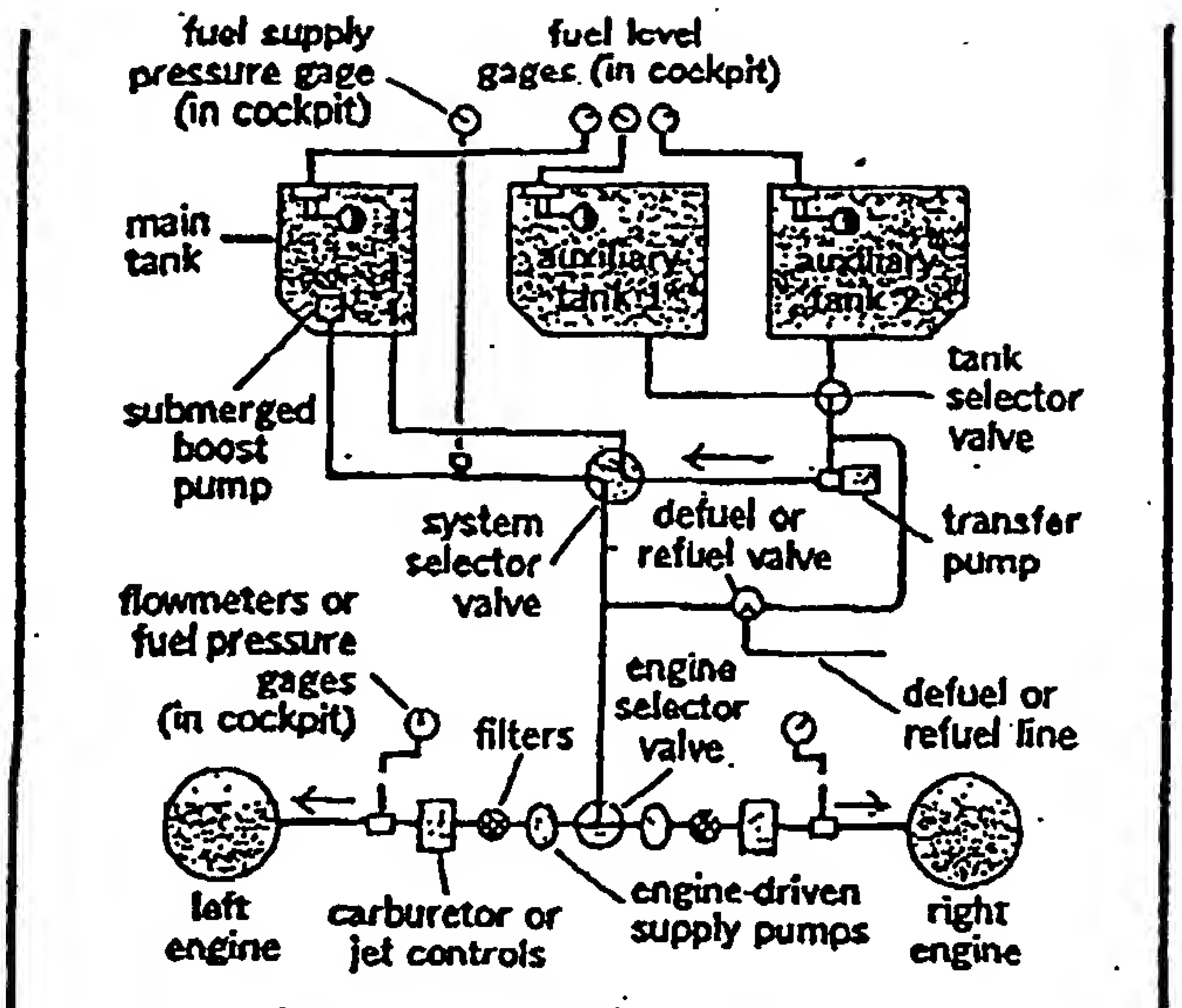


Diagram of a typical aircraft fuel system.

is usually such that all the fuel supply will pass to the engines by way of the main tank, which is refilled as necessary from the auxiliary tanks. In case of emergency, the system selector valve may connect the auxiliary tanks to the engines directly. [F.C.M./J.A.B.]

Fugacity A function introduced by G. N. Lewis to facilitate the application of thermodynamics to real systems. Thus, when fugacities are substituted for partial pressures in the mass action equilibrium constant expression, which applies strictly only to the ideal case, a true equilibrium constant results for real systems as well.

The fugacity f_i of a constituent i of a thermodynamic system is defined by the following equation (where μ_i is the chemical

$$\mu_i = \mu_i^* + RT \ln f_i$$

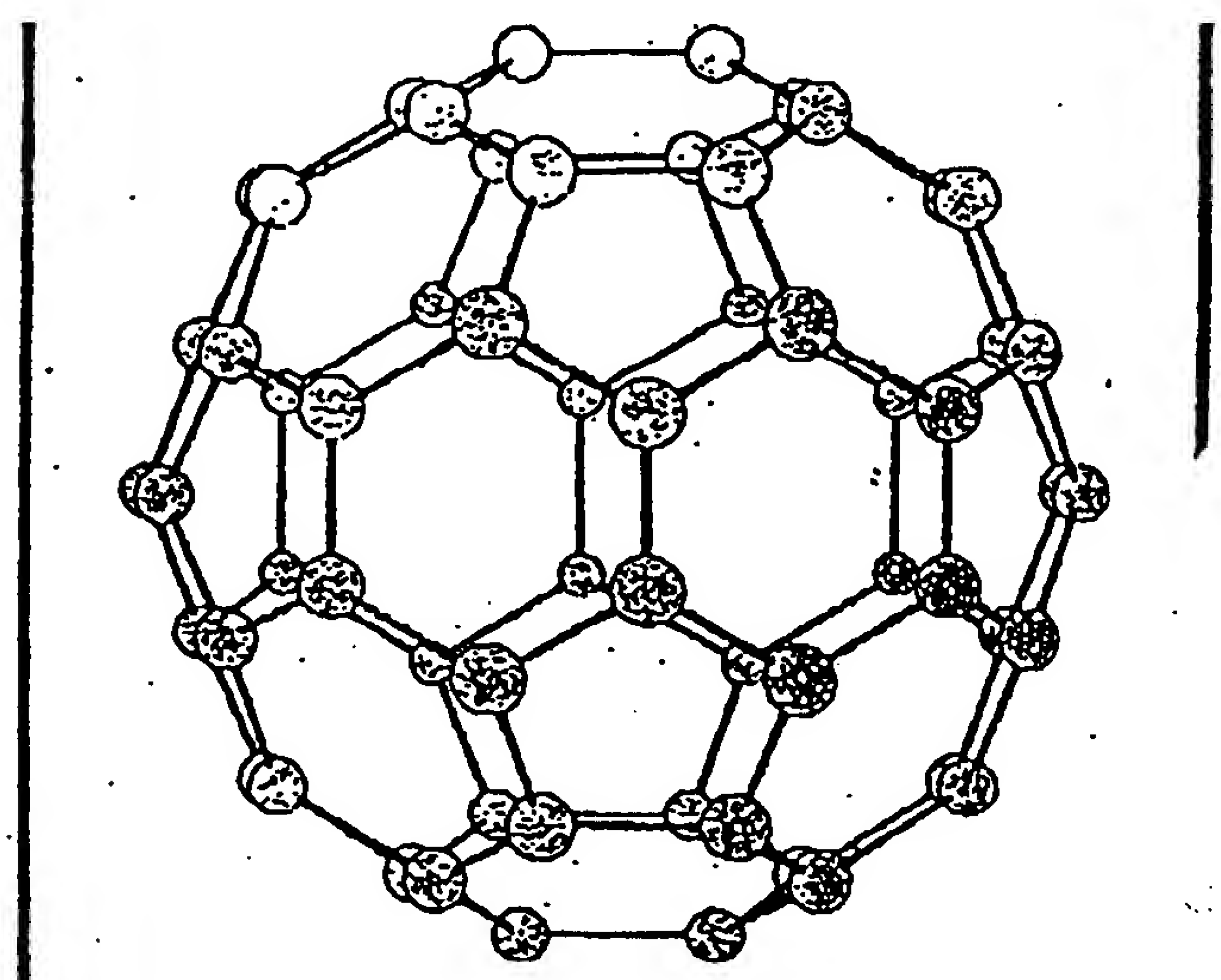
potential and μ_i^* is a function of temperature only), in combination with the requirement that the fugacity approach the partial pressure as the total pressure of the gas phase approaches zero. At a given temperature, this is possible only for a particular value for μ_i^*, which may be shown to correspond to the chemical potential the constituent would have as the pure gas in the ideal gas state at 1-atm pressure. This definition makes the fugacity identical to the partial pressure in the ideal gas case. For real gases, the ratio of fugacity to partial pressure, called the fugacity coefficient, will be close to unity for moderate temperatures and pressures. At low temperatures and appropriate pressures, it may be as small as 0.2 or less, whereas at high pressures at any temperature it can become very large. See ACTIVITY (THERMODYNAMICS); CHEMICAL EQUILIBRIUM; CHEMICAL THERMODYNAMICS; GAS. [P.J.B.]

Fullerene A molecule containing an even number of carbon atoms arranged in a closed hollow cage. The fullerenes were discovered as a consequence of astrophysically motivated chemical physics experiments that were interpreted by using geodesic architectural concepts. Fullerene chemistry, a new field that appears to hold much promise for materials development and other applied areas, was born from pure fundamental science. See CARBON.

In 1985, fifteen years after it was conceived theoretically, the molecule buckminsterfullerene (C_{60} or fullerene-60) was discovered serendipitously. Fullerene-60 (see illustration) is the archetypal member of the fullerenes, a set of hollow, closed-cage molecules consisting purely of carbon. The fullerenes can be considered, after graphite and diamond, to be the third well-defined allotrope of carbon.

In the fullerene molecule an even number of carbon atoms are arrayed over the surface of a closed hollow cage. Each atom is trigonally linked to its three near neighbors by bonds that delineate a polyhedral network, consisting of 12 pentagons and n hexagons. All 60 atoms in fullerene-60 are equivalent and lie on the surface of a sphere distributed with the symmetry of a truncated icosahedron. The 12 pentagons are isolated and interspersed symmetrically among 20 linked hexagons; that is, the symmetry is that of a modern soccerball. The molecule was named after R. Buckminster Fuller, the inventor of geodesic domes, which conform to the same underlying structural formula. Three of the four valence electrons of each carbon atom are involved in the sp^2 sigma-bonding skeleton, and the fourth p electron is one of 60 involved in a pi-delocalized molecular-orbital electron sea that covers the outside (exo) and inside (endo) surface of the molecule. The resulting cloud of pi electron density is similar to that which covers the surface of graphite; indeed, the molecule can be considered a round form of graphite. See ELECTRON CONFIGURATION; GRAPHITE.

Fullerene-60 behaves as a soft electrophile, a molecule that readily accepts electrons during a primary reaction step. It can accept three electrons readily and perhaps even more. The molecule can be multiply hydrogenated, methylated, ammonated, and fluorinated. It forms exohedral complexes in which an atom (or group) is attached to the outside of the cage, as well as endohedral complexes in which an atom [for example, lanthanum (La), potassium (K), or calcium (Ca)] is trapped inside the cage.

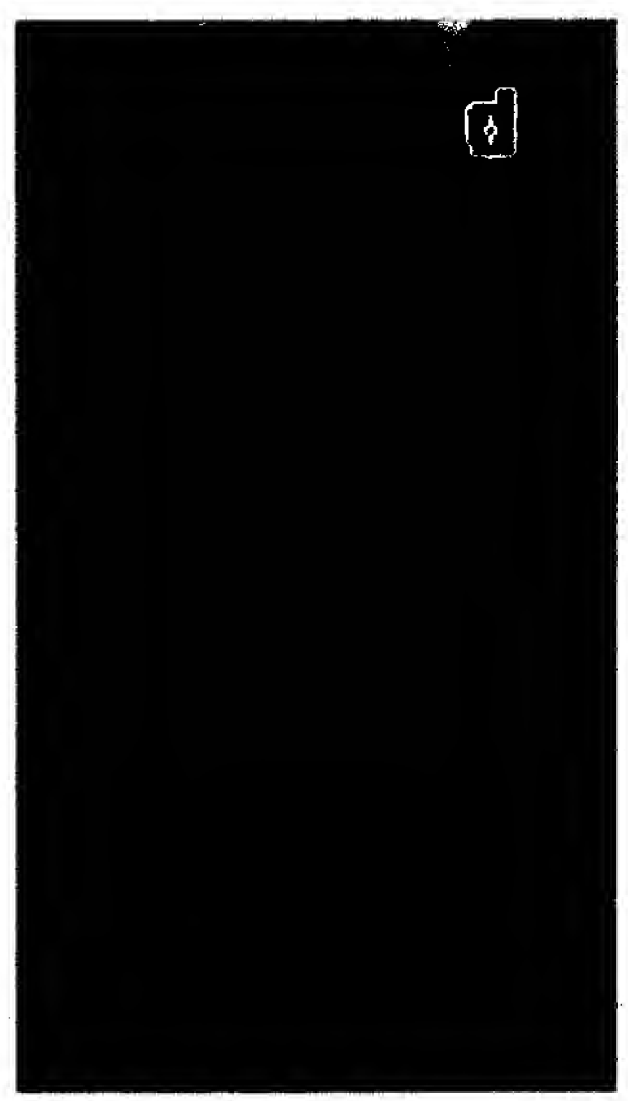

Structure of C_{60} (buckminsterfullerene).

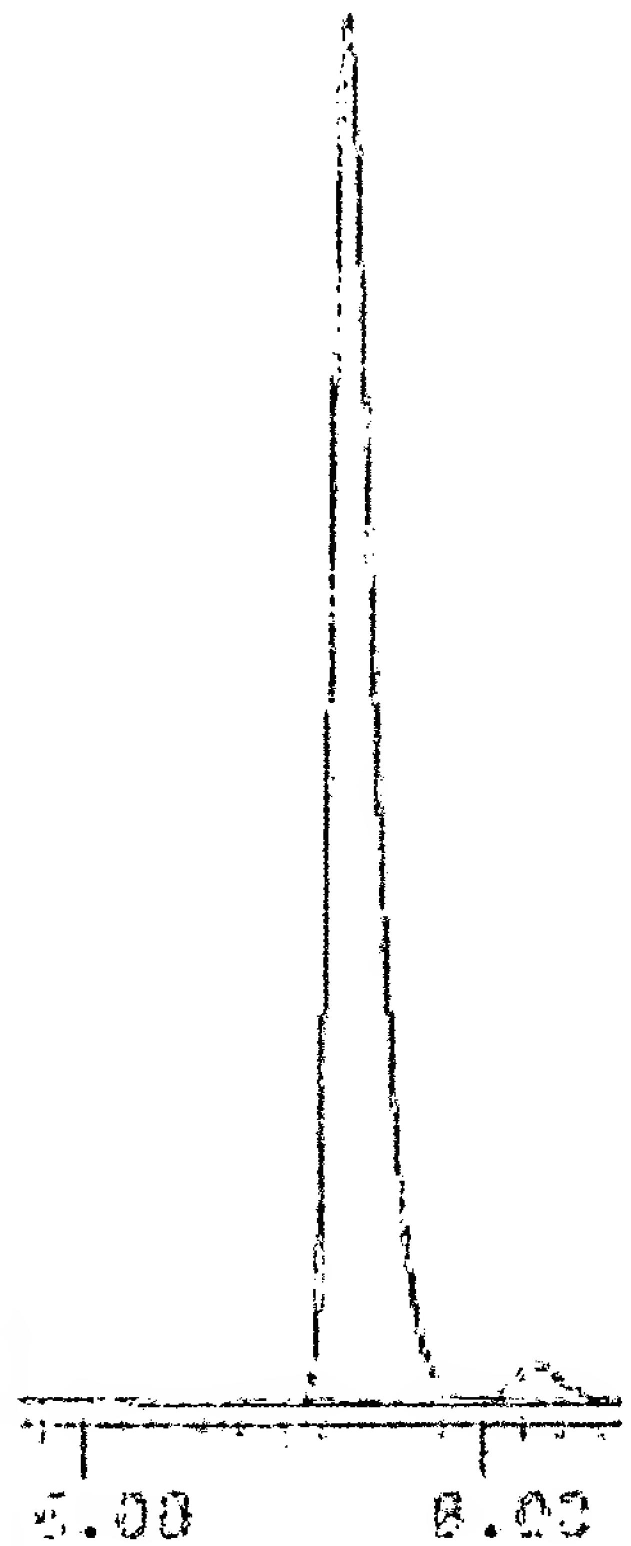
Fullerene materials have been available for such a short time that applications are yet to be established. However, the properties already discovered suggest that there is likely to be a wide range of areas in which the fullerenes or their derivatives will have uses.

Fullerene-60 was discovered as a direct result of physicochemical investigations that simulated processes occurring in stars and in space. Consequently the likelihood that fullerenes, in particular fullerene-60, and analogs are present in space is a fascinating conjecture. [H.W.K.]

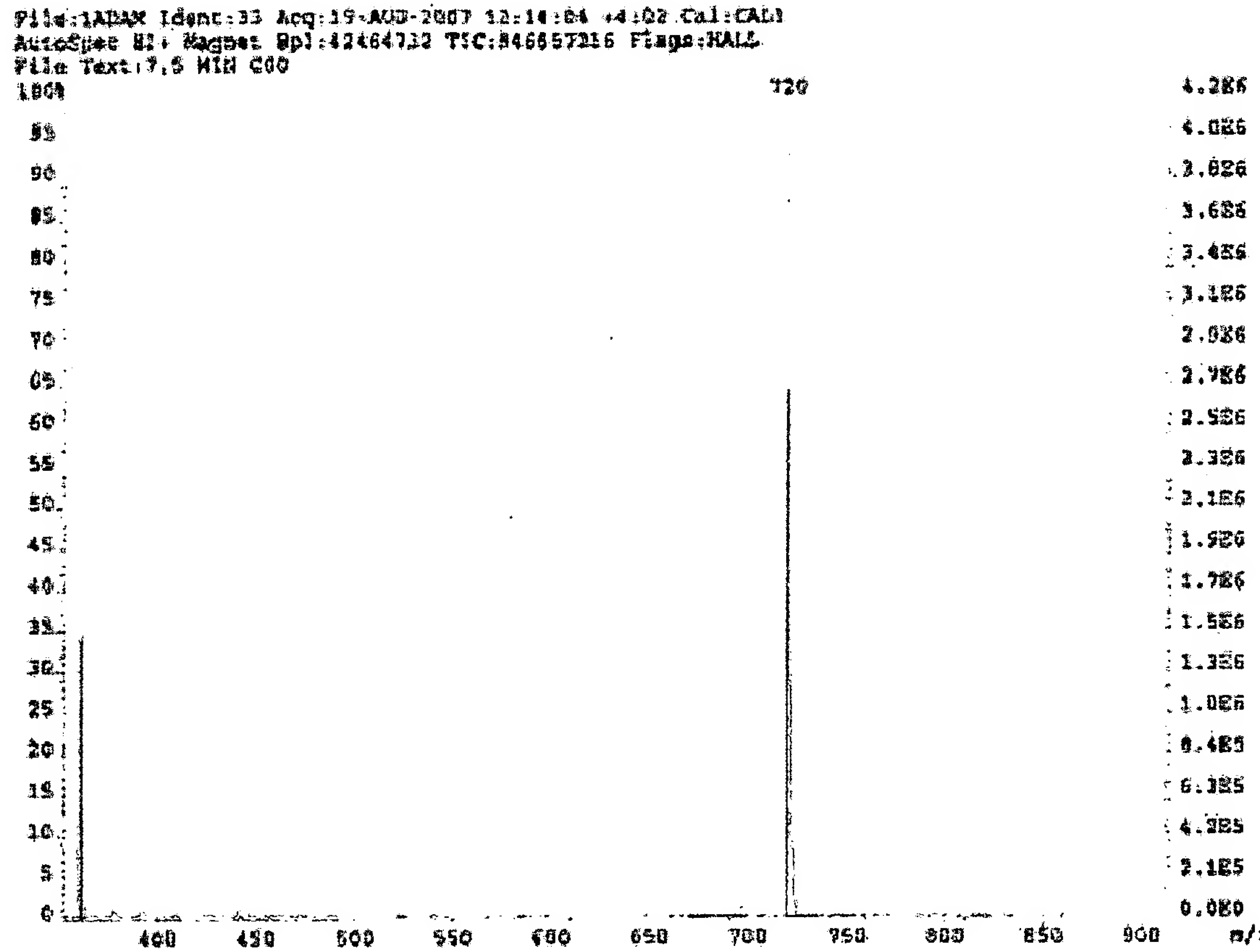
Fuller's earth Any natural earthy material (such as clay materials) which decolorizes mineral or vegetable oils to a sufficient extent to be of economic importance. It has no mineralogic significance. The clay minerals present in fuller's earth may include montmorillonite, attapulgite, and kaolinite.

c





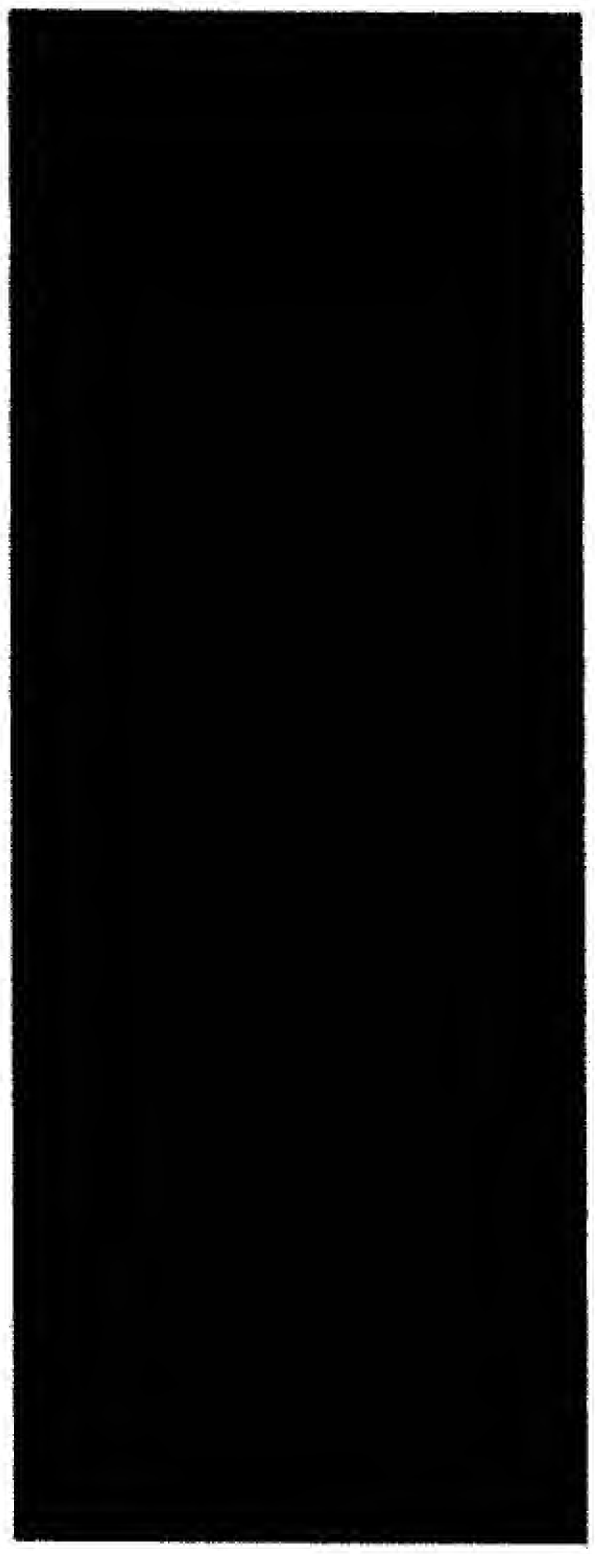
b

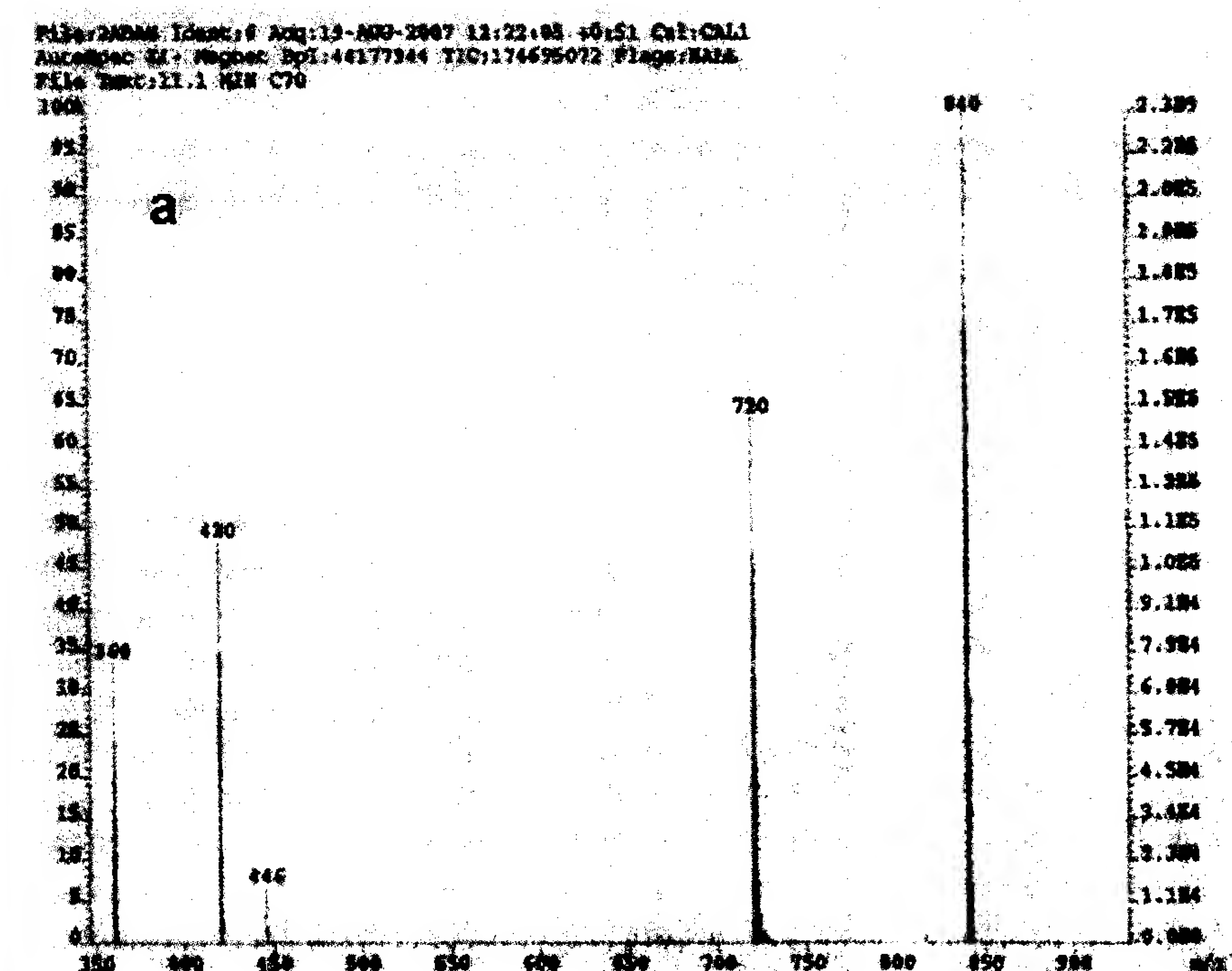


a

a. Mass spectra of C_{60}
b. HPLC traces (7.5 minute)
c. C_{60} solution in toluene
d. C_{60} crystals

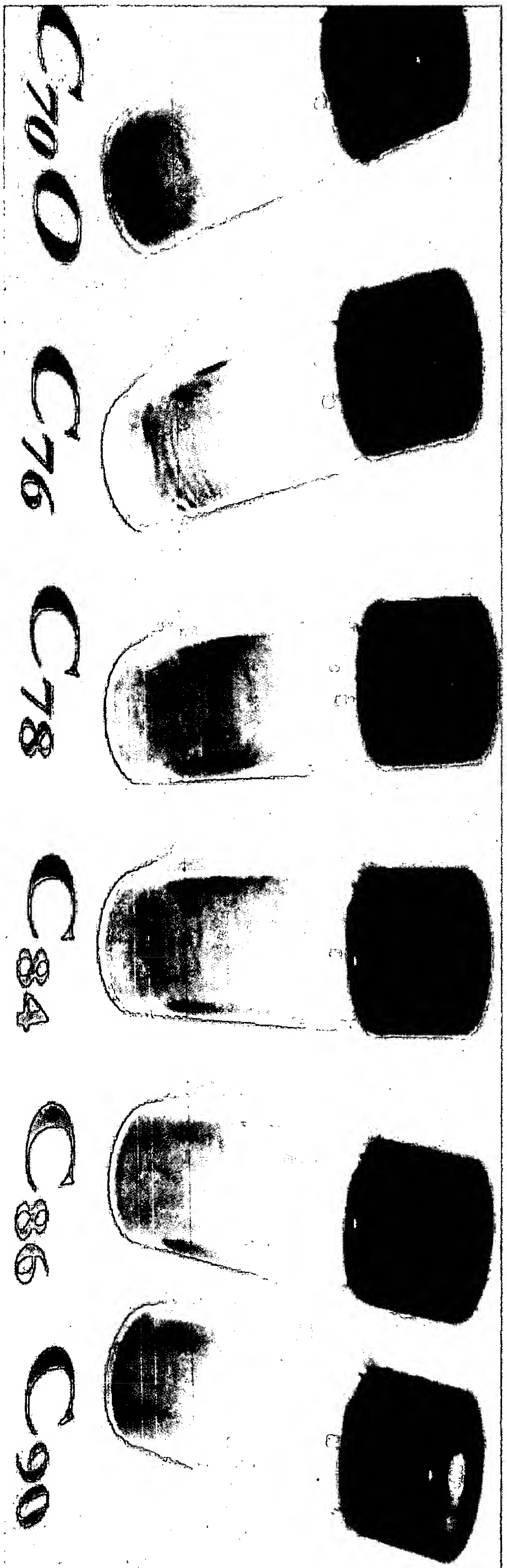
c

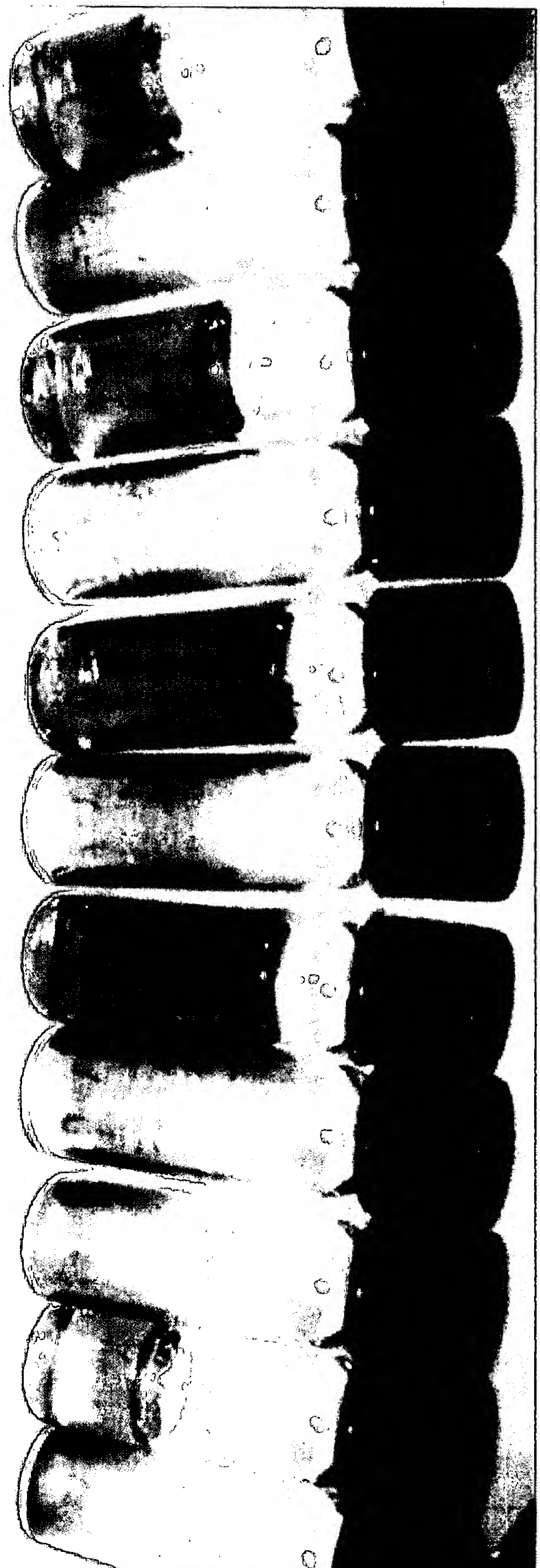




a. Mass spectra of C_{70}
b. HPLC traces (11.1 minutes)
c. C_{70} solution in toluene
d. C_{70} crystals

KROTO EXHIBIT 5





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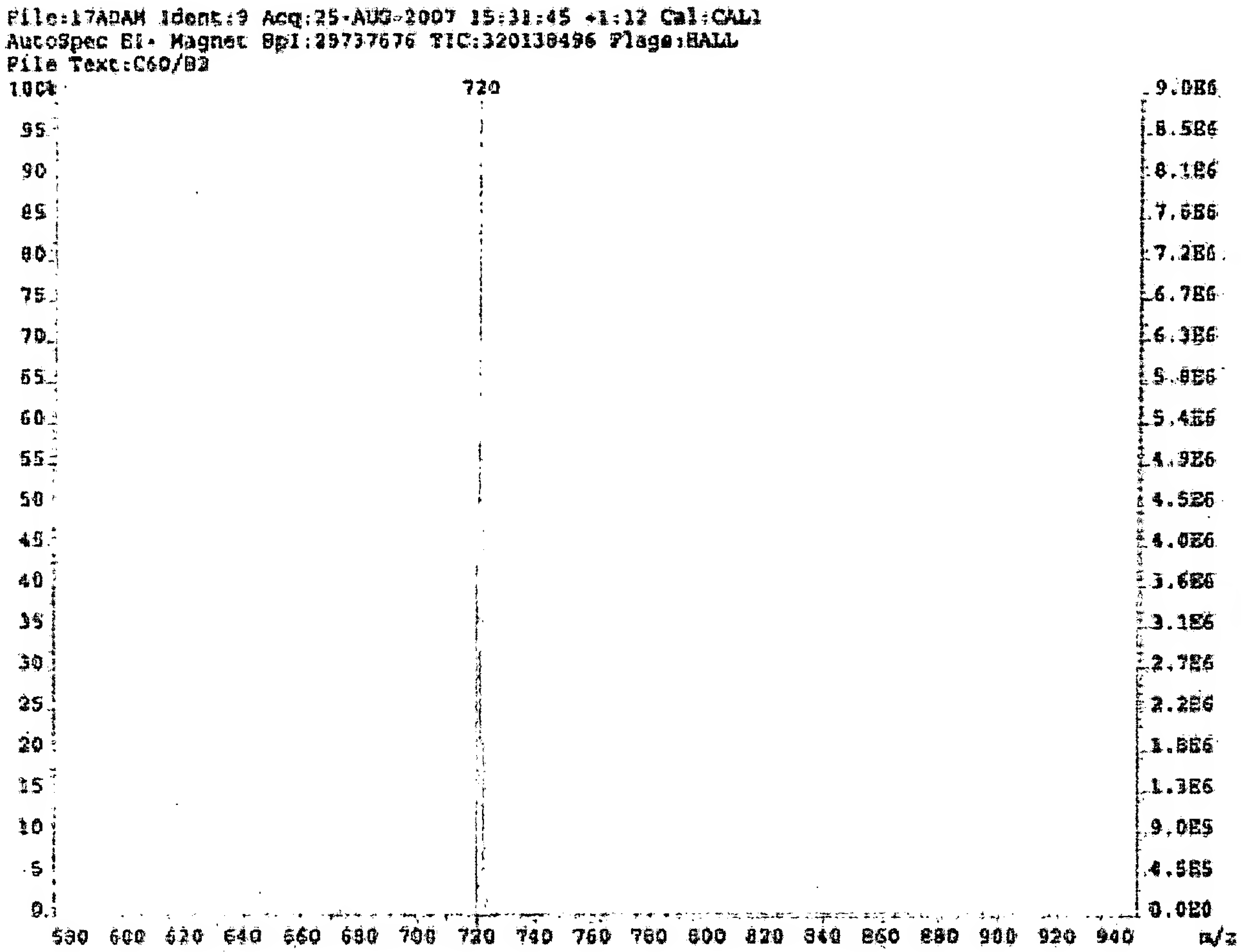
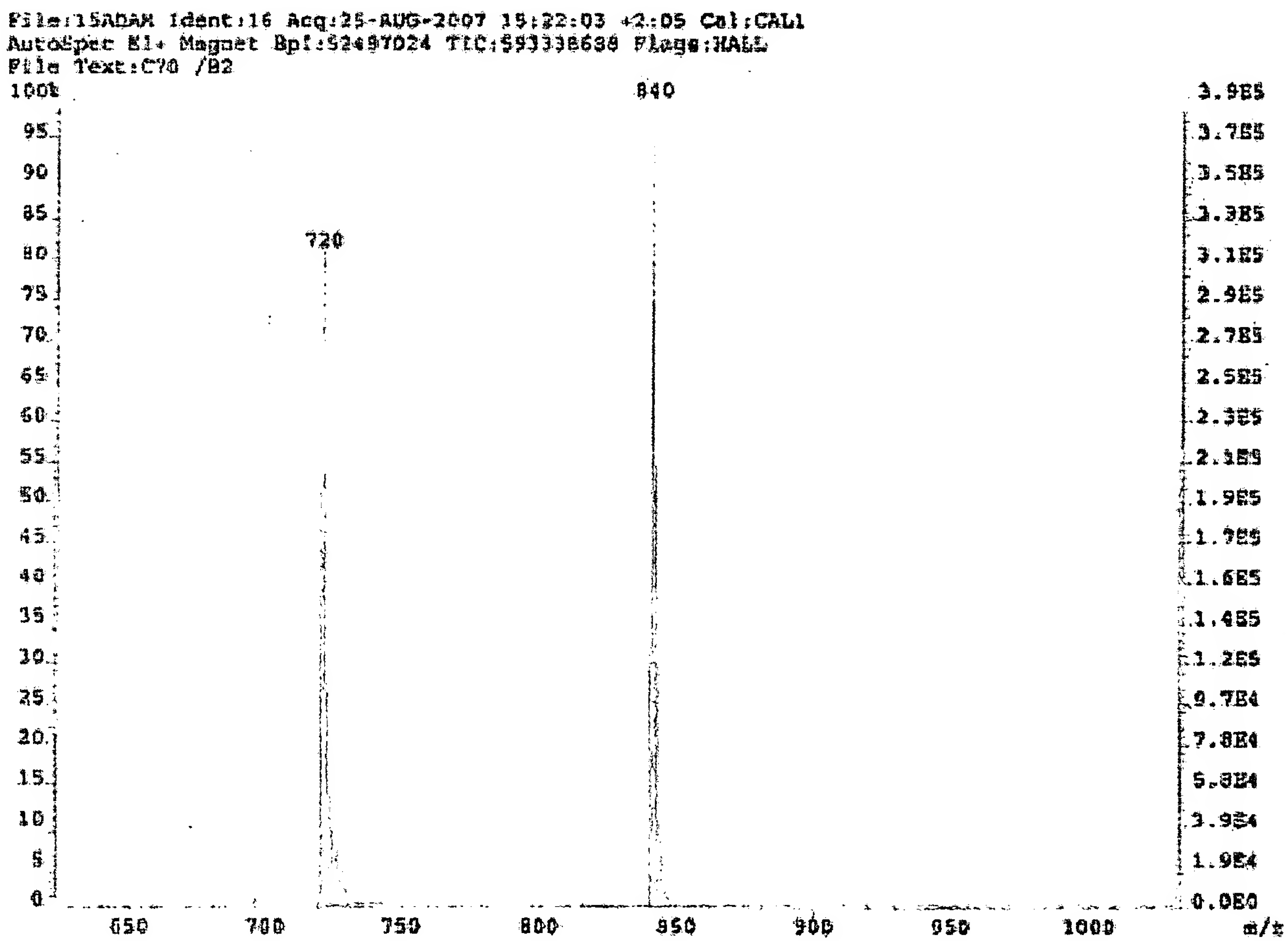


Mass spectra of C_{60}

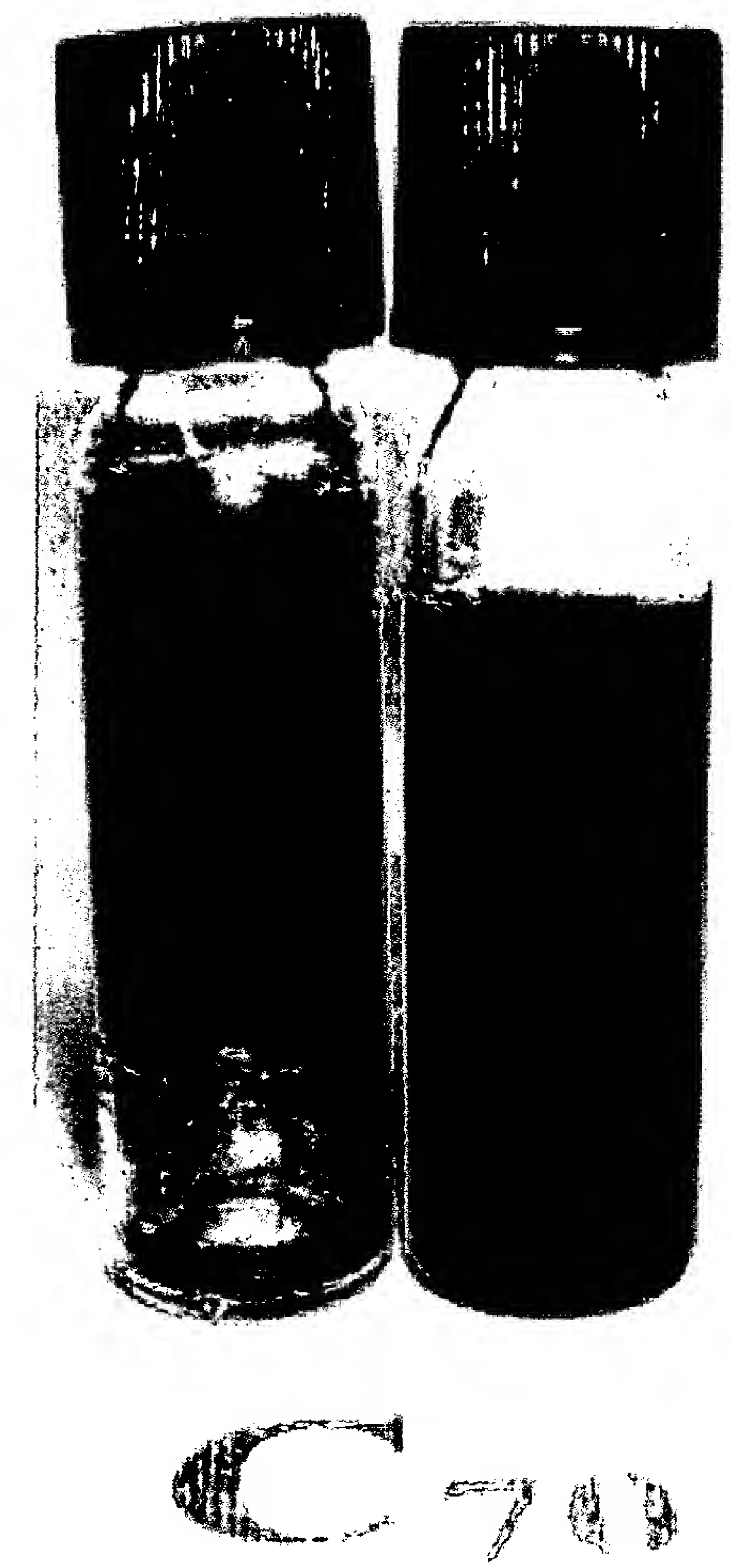
C_{60} solution in toluene
C_{60} crystals

KROTO EXHIBIT 7

KROTO EXHIBIT 8

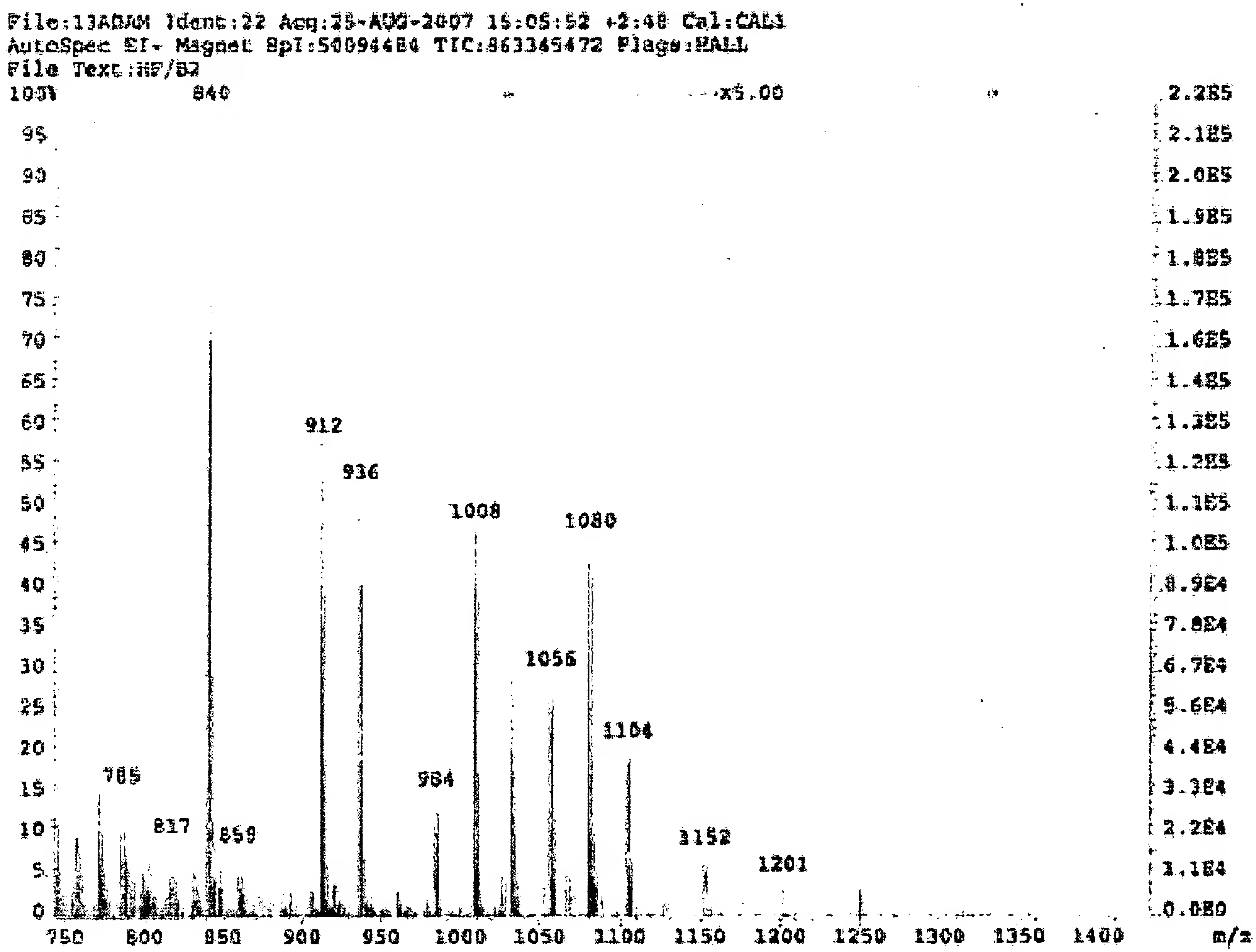


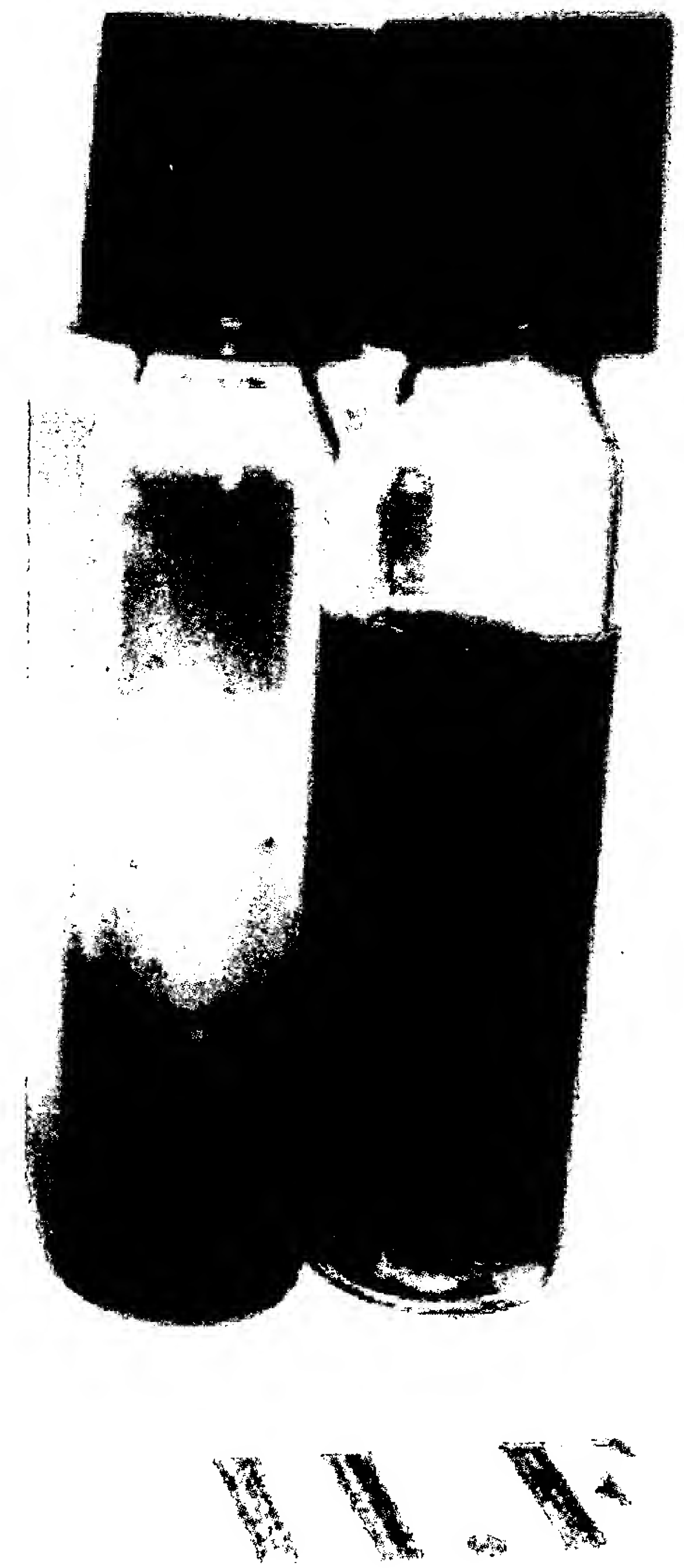
Mass spectra of C_{70}



C_{70} solution in toluene
C_{70} crystals

KROTO EXHIBIT 9





Mass spectra of H.F's up to C_{104}

H.F's solution in toluene
H.F's crystals


C60
C70
H.F
Batch 2

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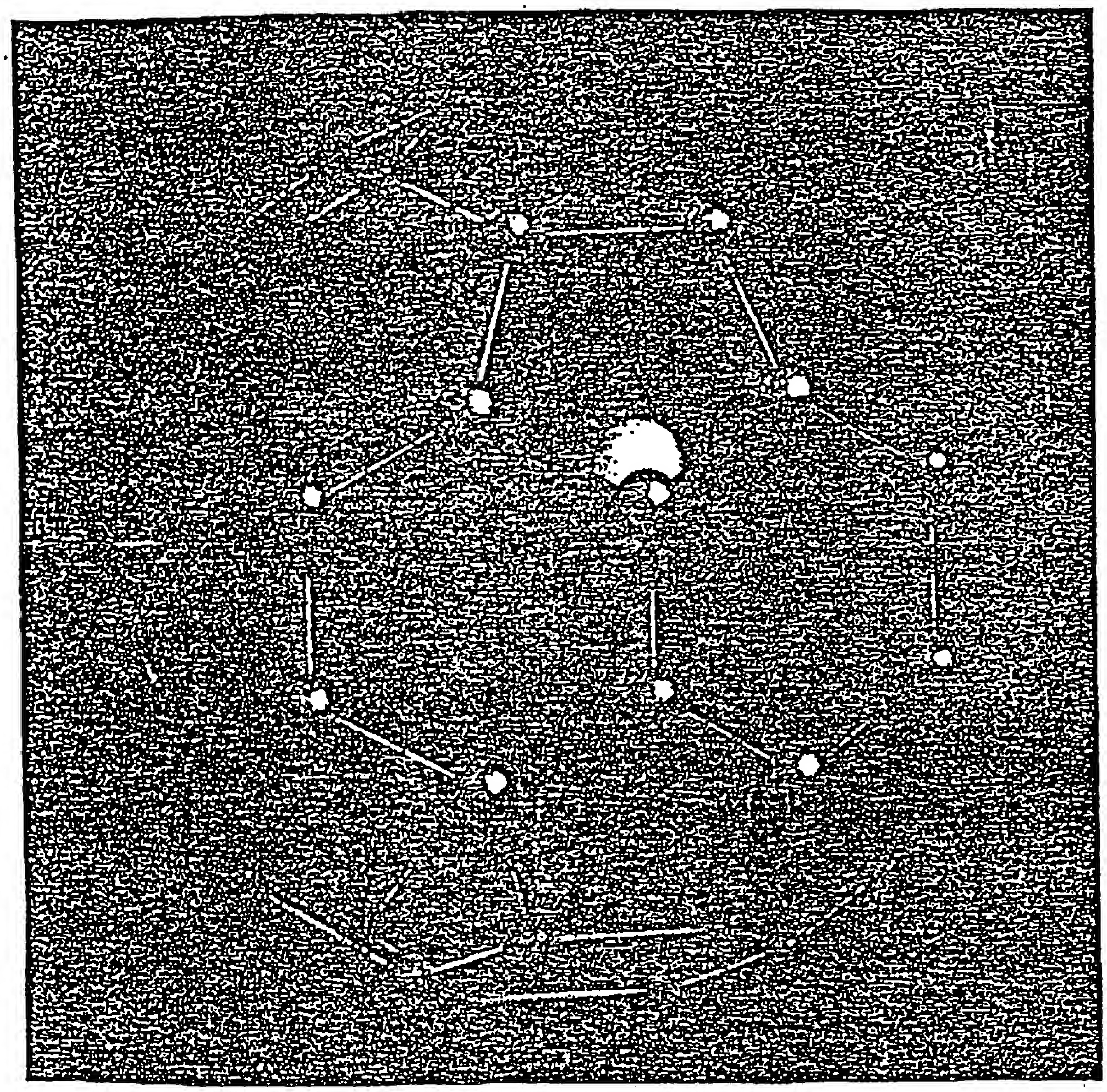
Remnants of a planet that failed to form.

Still no technological fix for oil spills.

What made higher life-forms possible?



Buckyball, the third form of pure carbon, cages an atom in its lattice.

KROTO EXHIBIT 11

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Fullerenes

These cagelike molecules constitute the third form of pure carbon (the other two are diamond and graphite). C_{60}, the archetype, is the roundest molecule that can possibly exist

by Robert F. Curl and Richard E. Smalley

In May of 1990 Wolfgang Krätschmer and his student Konstantinos Fostiropoulos carefully mixed a few drops of benzene with a specially prepared carbon soot. The clear solvent turned red.

Excitedly, the two workers for the Max Planck Institute for Nuclear Physics in Heidelberg telephoned their collaborators, Donald Huffman and Lowell Lamb of the University of Arizona in Tucson, who quickly repeated the experiment. The excitement continued as the two groups communicated daily by telephone and fax, exchanging measurements of the material—its infrared and ultraviolet spectra, its X-ray diffraction pattern and its mass spectrograph. Yes, the values all matched those predicted for the 60-atom carbon cluster buckminsterfullerene.

Even though some theorists had argued that this hollow, soccerball-shaped molecule should be detectable in abundance in such everyday circumstances as a candle flame, the German-American team had actually found it, succeeding where all others had failed. They were the first to observe this roundest of all round molecules, and they knew that chemistry books and encyclopedias would never be quite the same. Now there were three known forms of pure carbon: the network solids, diamond and graphite, and a new class of discrete molecules—the fullerenes.

When we heard of this breakthrough a few months later in Texas, we celebrated with champagne all around. For although we had to some extent been scooped, we had been vindicated as well. Five years earlier we had had our own Eureka! experience. Together with our colleague Harold W. Kroto of the University of Sussex and our students James R. Heath and Sean C. O'Brien, we had found that C_{60} could be made in a uniquely stable form simply by laser-vaporizing graphite in a pulsed jet of helium. We had gone on to propose that this extraordinary stability could be explained by a molecular structure having the perfect symmetry of a soccerball. Because the architectural principle also underlies the geodesic dome invented by the American engineer and philosopher R. Buckminster Fuller, we named it buckminsterfullerene, or buckyball for short.

In addition to C_{60}, another molecule, C_{70}, appeared to be quite special in these early experiments. We soon found that the stability of C_{70} could be understood if the molecule had also taken the form of a geodesic dome. As Fuller had pointed out, all such domes can be considered networks of pentagons and hexagons. The 18th-century Swiss mathematician Leonhard Euler calculated that any such object must have precisely 12 pentagons in order to close into a spheroid, although the number of hexagons can vary widely. The soccerball structure of C_{60} has 20 hexagons, whereas the structure we proposed for C_{70} has 25, producing a shape reminiscent of a rugby ball.

In fact, we had found that all the even-numbered carbon clusters greater than about 32 atoms in size were remarkably stable (although less so than 60 or 70), and the evidence soon led us to postulate that all these molecules had taken the structure of geodesic domes. Again, in honor of Fuller, it seemed fitting to term this entirely new class of molecules the "fullerenes."

We later learned that such molecules had already been imagined. David E. H. Jones, writing under the pseudonym "Daedalus" in the *New Scientist* in 1966, had conceived of a "hollow molecule" made of curled-up graphitic sheets. Others had predicted the stability of C_{60} from calculations and tried—unsuccessfully—to synthesize it. We, however, were apparently the first to discover that the material could form spontaneously in a condensing carbon vapor.

Although our evidence was sound and our conclusions were supported by extensive further experiments and theoretical calculations, we could not collect more than a few tens of thousands of these special new molecules. This amount was plenty to detect and probe with the sophisticated techniques available in our laboratory, but there was not enough to see, touch or smell. Our evidence was indirect, much as it is for physicists who study antimatter. For now, the fullerenes existed only as fleeting signals detected in our exotic machines. But as chemists, we knew that the new material ought to be perfectly stable. Unlike antimatter, the geodesic forms of carbon should be quite safe to hold in one's bare hand. All we had to do was make more of them—billions and billions more.

Thus, for five years, we had been searching for a method of producing visible amounts of the stuff. We called our efforts "the search for the yellow vial" because quantum calculations for such a soccerball-shaped carbon molecule suggested it would absorb light strongly only in the far violet part of the spectrum. We were not alone. Our initial "soccerball"

ROBERT F. CURL and RICHARD E. SMALLEY of Rice University have collaborated for the past seven years in research on carbon and semiconductor clusters in supersonic beams. Curl is a professor in, and chairman of, the department of chemistry. Smalley is the Gene and Norman Hackerman Professor of Chemistry and a professor of physics. For the past five years, he has also served as the chairman of the Rice Quantum Institute.

HYPERFULLERENE STRUCTURE called a Russian egg is expected to form along with ordinary fullerenes in a laser-vaporized carbon plume. Shown here is the most symmetric form: a C_{60} at the core is encapsulated by fullerenes having 240, 540 and 960 atoms. This process could continue indefinitely to produce a macroscopic particle whose pentagons are in icosahedral alignment.

proposal, published in *Nature* in 1985, had made the quest one of the hottest in chemistry.

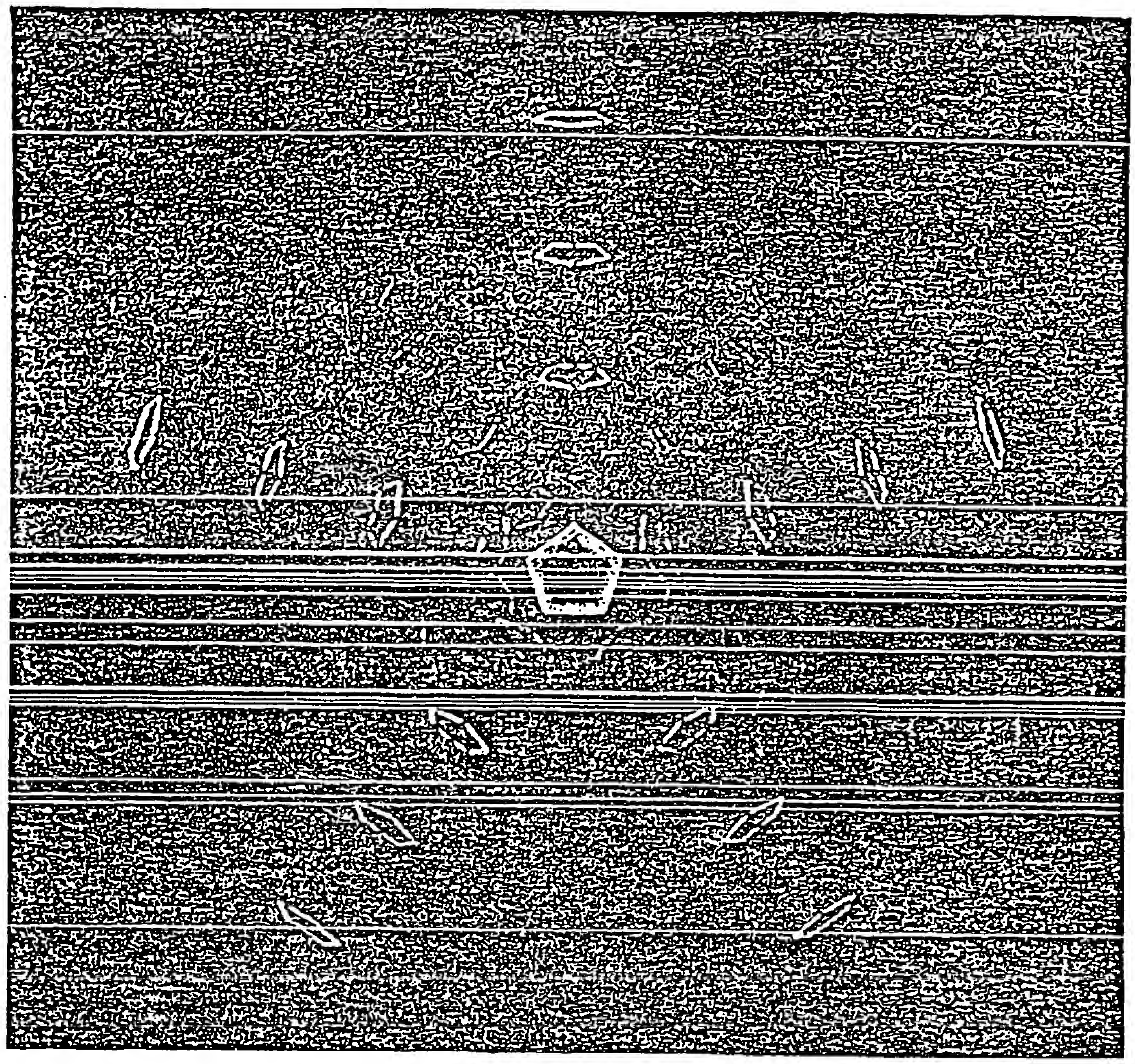
In our laboratory we collected the sooty carbon produced by the vaporization laser while using various chemical techniques to detect the presence of C_{60}. We slurried the soot in benzene, for example, and looked for a yellow color. But the solution in our test tubes stayed clear, with boring black soot sitting on the bottom. The community of cluster chemists ran many more sophisticated experiments but achieved no better result.

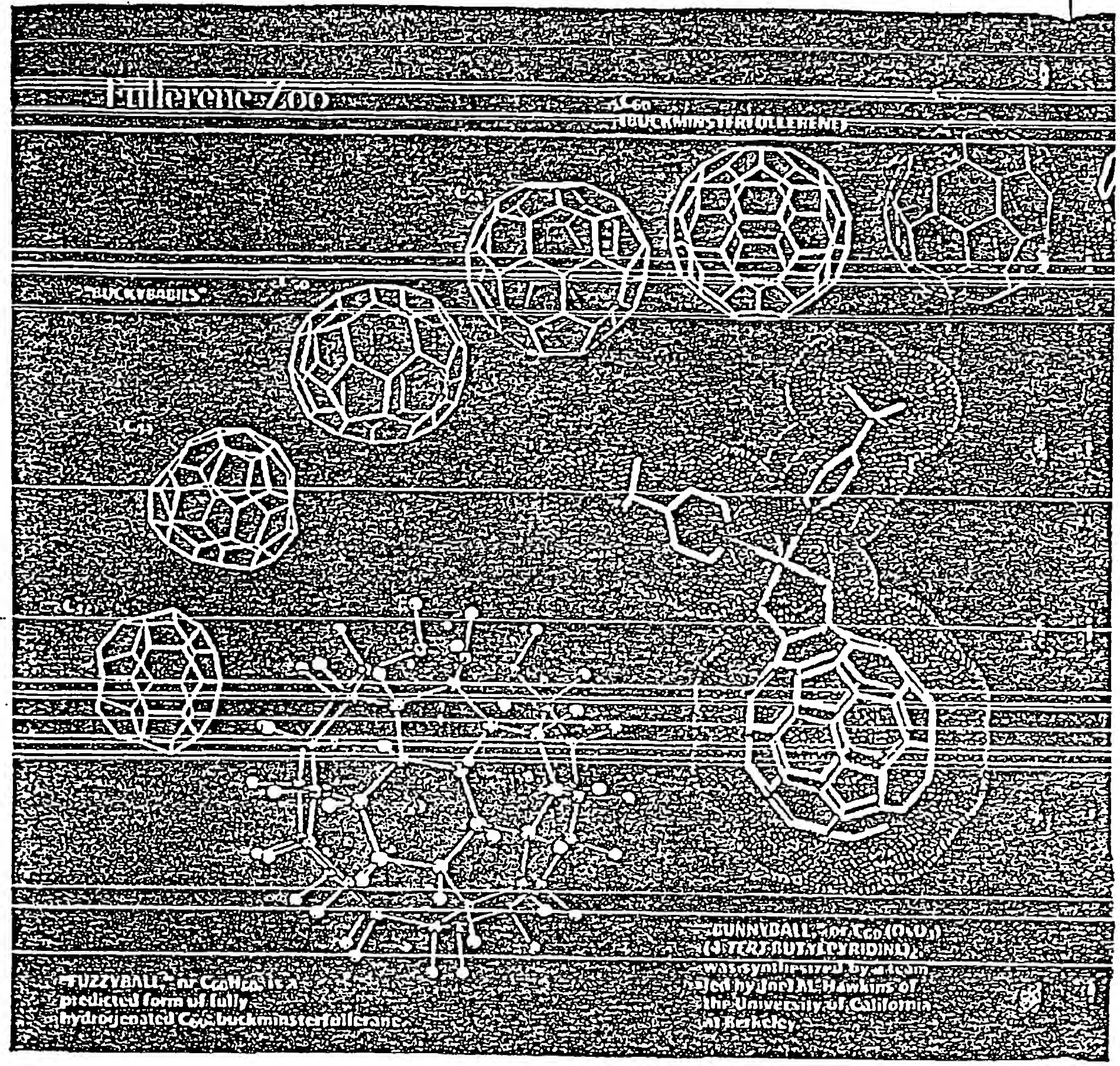
Many gave up hope of ever seeing the yellow vial. They reasoned that although the fullerenes may be stable, it was too hard to separate them from the other sooty material being produced in the vaporization experiments. Perhaps, the workers said, some dedicated chemist might one day extract a few micrograms with some special solvent, but no one seriously expected C_{60} to be available in bulk anytime soon.

In the end, the breakthrough was made not by chemists but by physicists working in a totally different area. Huffman, Krätschmer and their students had been engaged for decades in a study of interstellar dust, which they assumed to consist mainly of particles of carbon (the most common particle-forming element). They therefore modeled the phenomenon in the laboratory by vaporizing carbon and condensing it in as many ways as possible. Optical tests figured in most of the studies. (Virtually all that is known of the interstellar dust stems from observations of how it absorbs and scatters starlight.)

In 1983 the physicists tried evaporating a graphite rod by resistive heating in an atmosphere of helium. They noticed that when the helium pressure was just right (about a seventh of an atmosphere), the dust strongly absorbed wavelengths in the far ultraviolet region, creating a peculiar, double-humped spectrum [*see bottom illustration on page 58*]. Most observers would have missed the two blips on the screen, but not Huffman and Krätschmer: they had studied spectra of carbon dust for years without encountering such an effect. They dubbed it their "camel" sample and wondered what it meant.

Nearly three years later, in the late fall of 1985, Huffman read in *Nature* of





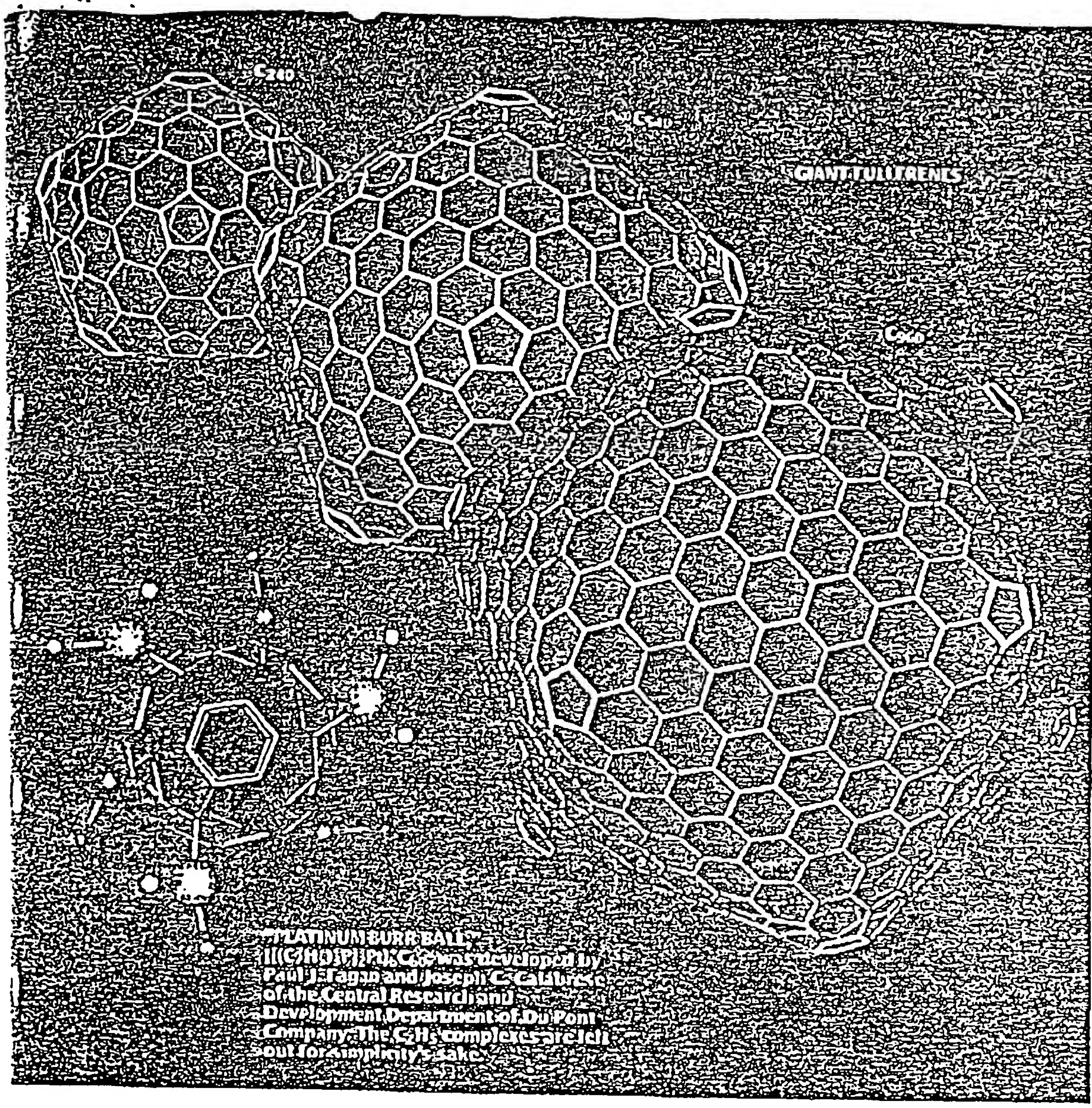
"FUZZYBALL," or $C_{60}H_{60}$, is a predicted form of fully hydrogenated C_{60} buckminsterfullerene.

"BUNNYBALL," or $C_{60}(OsO_4)$(4-TERT-BUTYLPYRIDINE)$_2$, was synthesized by a team led by Joel M. Hawkins of the University of California at Berkeley.

our discovery of C_{60} and began to wonder if a hollow soccerball molecule might be the cause of the double hump. Yet this explanation seemed too good to be true, for it required that C_{60} account for a significant portion of the sample. Why would so much of the carbon end up in such perfectly symmetric cages? What did the helium do to make it possible? The seeming unlikeliness of this hypothesis, together with some difficulty in reproducing the experiment, led the researchers to put the project on the back burner.

By 1989, however, Huffman and Krätschmer had become convinced that the C_{60} hypothesis ought to be reexamined. They renewed their interest in the camel sample, readily reproducing the results of the 1983 experiments. This time their attention turned to measuring the sample's absorption of infrared light—the wavelengths that interact with the vibrational motion of molecules—in order to test the results against theoretical predictions that had by now been made for soccerball C_{60}. These predictions held that of the 174 vibrational modes of this putative molecule, only 46 would be distinct, and only four would appear in the infrared range. To their surprise, they found the camel sample did display four sharp infrared absorption lines, and they verified that the lines were present only in carbon dust produced in the special camel way. This finding provided striking evidence that C_{60} might be present in abundance.

Influenced by their background in physics, the workers initially chose to test their hypothesis by a rather in-



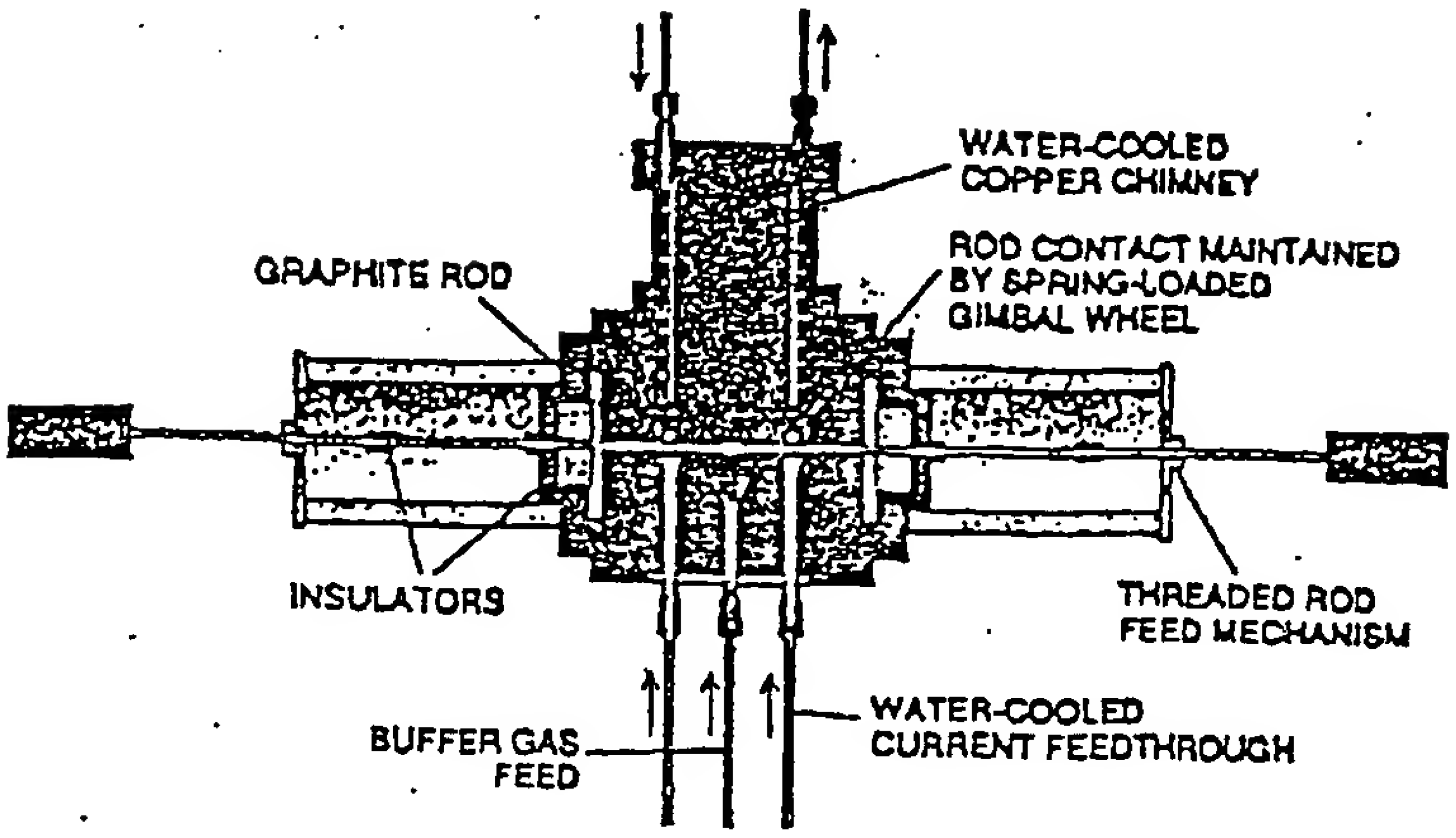
"PLATINUM BURR BALL," $[(C_2H_5)_3P]_6Pt_6C_{60}$ was developed by Paul J. Fagan and Joseph C. Calabrese of the Central Research and Development Department of Du Pont Company. The C_2H_5 complexes are left out for simplicity's sake.

volved route. They prepared a sample from pure ^{13}C, a heavy isotope of carbon, and verified that the extra mass shifted the four infrared bands in the way expected for so large a molecule composed exclusively of carbon. Ultimately, however, they realized that the simplest assay followed a basic dictum of organic chemistry: like dissolves like. Should their sample dissolve in an aromatic solvent, such as benzene, this would support the predicted aromaticity of C_{60}. Because benzene molecules take the shape of a ring of carbon atoms, C_{60} would thus be seen as a kind of spherical benzene.

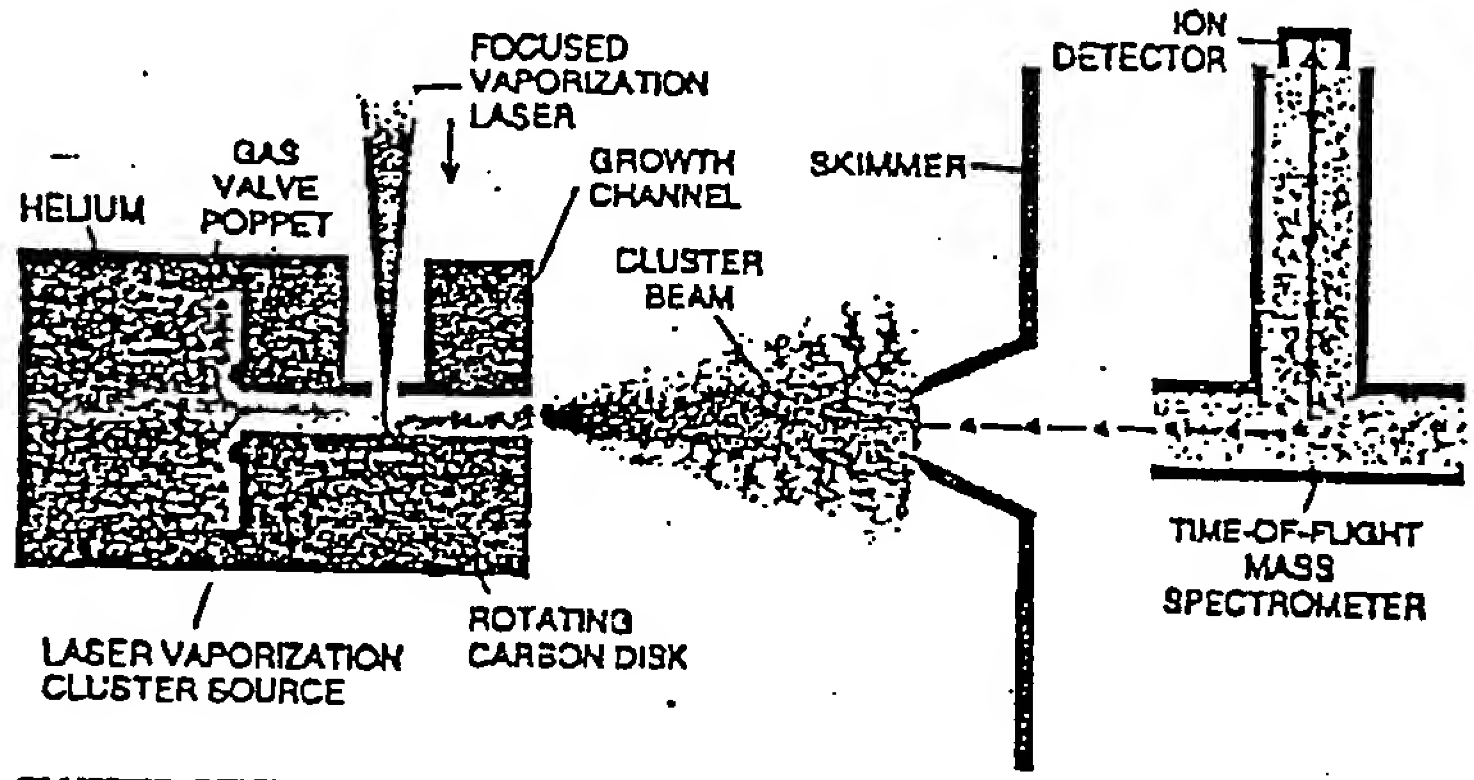
When the Krätschmer-Huffman group finally added benzene to their camel sample and saw the color red develop, they realized they were looking at the first concentrated solution of fullerenes ever seen. They evaporated the solvent and found that tiny crystals remained, which readily redissolved. These crystals could be sublimed under a vacuum near 400 degrees Celsius and condensed on a cold microscope slide to form smooth films of solid materials, which Krätschmer and Huffman christened "fullerite."

In thin layers these films were yellow (a fact that those of us at Rice University who searched for a "yellow vial" find highly gratifying). Although it took a while to obtain precise numbers, it is now known that carbon dust prepared in the camel way produces an extractable fullerene mixture made up of roughly 75 percent C_{60} (the soccer-ball), 23 percent C_{70} (the rugby ball) and a grab bag of larger fullerenes.

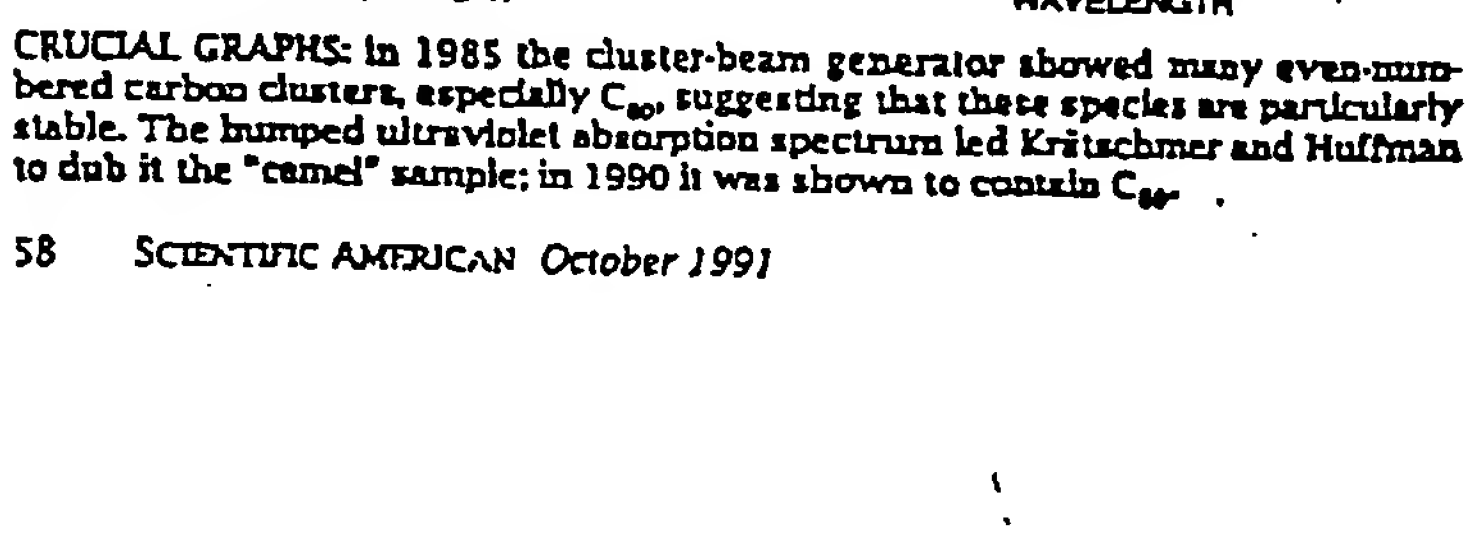
Here was a new form of pure, solid



FULLERENE FACTORY makes macroscopic samples in a carbon arc. The arc—a refinement of an apparatus developed by Wolfgang Krätschmer and Donald Huffman—frees carbon atoms that coalesce into sheets. Inert helium holds the sheets near the arc long enough for them to close in on themselves, forming fullerenes.



CLUSTER GENERATOR designed by one of the authors (Smalley) produced the first evidence that fullerenes can form from carbon vapor. A pulsed laser vaporizes carbon; a gust of helium then sweeps the vapor into a supersonic beam whose expansion cools the atoms, condensing them.



CRUCIAL GRAPHS: In 1985 the cluster-beam generator showed many even-numbered carbon clusters, especially C_{60}, suggesting that these species are particularly stable. The humped ultraviolet absorption spectrum led Krätschmer and Huffman to dub it the "camel" sample; in 1990 it was shown to contain C_{60}.

carbon. It is the only pure, finite form. The other two, diamond and graphite, are actually infinite network solids. In the real world, one usually deals with hunks of diamond cut out of larger bulk crystals. Under normal conditions, the surfaces of such a piece are instantly covered with hydrogen, which ties up the dangling surface bonds. Graphite is much the same. No piece of diamond, therefore, can ever be truly pure under normal conditions. The fullerenes, on the other hand, need no other atoms to satisfy their chemical bonding requirements on the surface. In this sense, the fullerenes are the first and only stable forms of pure, finite carbon.

Once the Krätschmer-Huffman results were announced at a conference in Konstanz, Germany, in early September 1990, the race was on. The study of C_{60} and the fullerenes had been the province of the few select groups that had something like our elaborate and expensive laser-vaporization cluster-beam apparatus. Now Krätschmer and Huffman had opened the field to anyone who could procure a thin rod of carbon, a cheap power supply, a bell-jar vacuum chamber and a few valves and gauges. Everybody could play.

Within a few months, many groups were making their own fullerenes. Physicists, chemists and materials scientists thus began an interdisciplinary feeding frenzy that continues to intensify as this article is being written [*see box on page 62*]. The key results have been quickly reproduced in over a dozen laboratories, some of which have applied alternative procedures of verification as well. Because fullerenes are readily soluble and vaporizable molecules that remain stable in air, they are perfectly suited to a wide range of techniques.

One of the most powerful techniques—nuclear magnetic resonance (NMR)—has confirmed the single most critical aspect of the soccerball structure: that all 60 carbon atoms have exactly the same relation to the whole. Only the truncated icosahedral structure we proposed for C_{60} arranges the atoms so symmetrically as to distribute the strain of closure equally. Such even distribution makes for great strength and stability. Indeed, that is why we proposed the structure in the first place: it explains the extraordinary stability of the 60-atom species.

Because C_{60} is the most symmetric molecule possible in three-dimensional Euclidean space, it is literally the roundest of round molecules. Edgeless, chargeless and unbound, the molecule spins freely, as NMR experiments show,

more than 100 million times a second. The NMR experiments also dramatically verify that C_{70} has the shape of a tiny rugby ball: at room temperature, it spins rapidly about its long axis, stopping its frantic motion only below the temperature of liquid air.

High-resolution electron microscopy revealed these little carbon balls one at a time—as predicted, they spanned a bit more than one nanometer (a billionth of a meter). Scanning tunneling microscopy showed that when C_{60} molecules are deposited on a crystalline surface, they pack as regularly as billiard balls. X-ray diffraction studies demonstrated that—as one would expect—C_{60} crystallizes in a face-centered cubic lattice, with the balls a little more than 10 angstroms apart [*see illustration on page 62*]. The crystals are as soft as graphite. When squeezed to less than 70 percent of their initial volume, calculations predict that they will become even harder than diamond. When the pressure is relieved, they are observed to spring back to their normal volume. Thrown against steel surfaces at speeds somewhat greater than 17,000 miles per hour (about the orbital speed of the U.S. space shuttle), they are incredibly resilient: they just bounce back.

We found that the most convenient way to generate fullerenes consists of setting up an arc between two graphite electrodes. We maintained a constant gap by screwing the electrodes toward each other as fast as their tips evaporated. The process worked best when the helium pressure was optimized and other gases, such as hydrogen and water vapor, were rigorously eliminated. Such measures produced yields of dissolvable fullerenes that typically ranged between 10 and 20 percent of the vaporized carbon. Yields as high as 45 percent have recently been reported.

The only irreducible cost appears to be that of the electricity needed to run the arc. But even the small bench-top generators we are now using in our laboratory provide electricity at a cost that amounts to only about five cents per gram of C_{60}. Recently it has been found that a sooting flame (such as that of a candle) can be used to produce substantial yields of C_{60}. In the long run, this may prove the cheapest way to make the material. When the first large-scale applications of fullerenes are found—perhaps in superconductors, batteries or microelectronics [*see box on page 62*]—the manufacturing cost of C_{60} will probably fall close to that of aluminum: a few dollars a pound. What had recently been described as the "most controversial molecule in the Cosmos" is well on its way to becoming a bulk commodity.

A host of questions arises out of this wonder. What exactly is the helium doing? How can such a perfectly symmetric molecule be formed with such high efficiency out of the chaos of a carbon arc? And, on a more personal level, where did we go wrong? Why did we, and all other chemists for that matter, fail in the search for the yellow vial? Our technique involved helium as well. What did the Krätschmer-Huffman team do that made such a big difference?

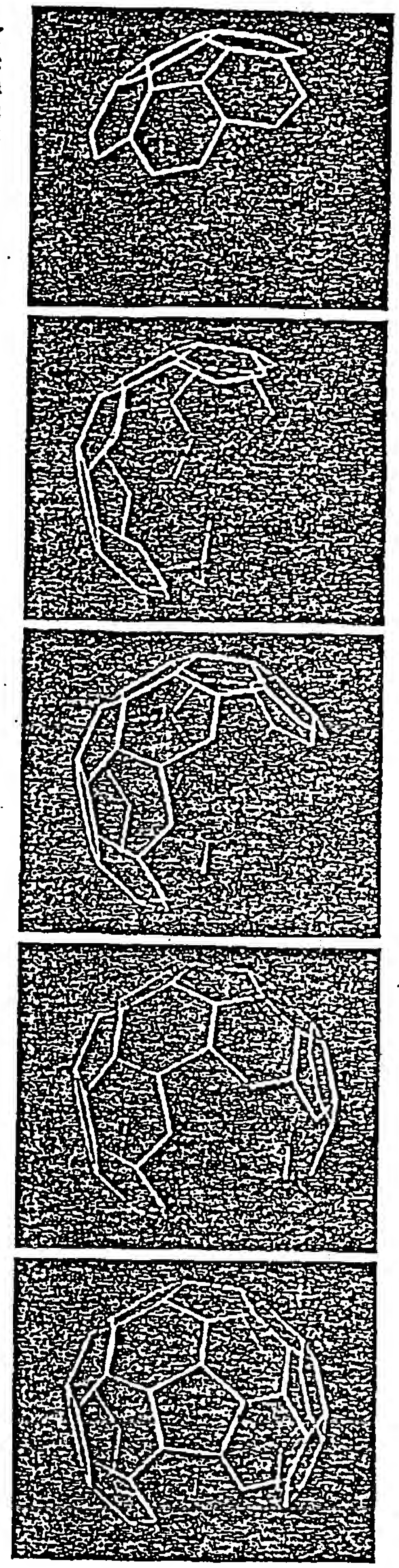
We now believe the answers to these questions lie in the way carbon vapor condenses at high temperatures. Linear carbon chains appear to link together to form graphitic sheets, and the sheets anneal as they grow in the hot vapor. Finally, stable, cagelike structures are favored by a key concept, which we call the pentagon rule.

Scientists had long known that when carbon is vaporized, most of its atoms initially coalesce into clusters ranging from two to 15 atoms or so. The very smallest carbon molecules are known to prefer essentially one-dimensional geometries. But clusters containing at least 10 atoms most commonly form a monocyclic ring—a kind of molecular Hula-Hoop that is especially favored at low temperatures. At very high temperatures, the rings break open to form units that comprise as many as 25 carbon atoms, taking the form of linear chains. Such chains might be imagined to look something like writhing snakes as they vibrate in the hot vapor.

It was these linear carbon chains that initially got us involved in carbon cluster studies and led to the discovery of C_{60}. Our British colleague, Harry Kroto, had theorized that the great abundance of such linear carbon chains in interstellar space may arise from chemical reactions in the outer atmospheres of carbon-rich red giant stars. In the early 1980s one of us (Smalley) had developed a supersonic cluster-beam device for the general study of small clusters composed of essentially any element in the periodic table [see "Microclusters," by Michael A. Duncan and Dennis H. Rouvray; SCIENTIFIC AMERICAN, December 1989].

We produced clusters by focusing an intense pulsed laser on a solid disk of the element to be studied. The local temperature could readily be brought above 10,000 degrees C—hotter than the surface of most stars and certainly hot enough to vaporize any known material. The resulting vapor was entrained in a powerful gust of helium, a chemi-

Growth of a Buckyball



cally inert carrier gas, which cooled the vapor so that it could condense into small clusters. As the carrier gas expanded through a nozzle into a vacuum, it generated a supersonic beam of clusters whose sizes could be measured by a mass spectrometer.

In 1984 a group at Exxon using a copy of the cluster-beam apparatus developed at Rice had been the first to study carbon clusters in this fashion. Their results strongly suggested that the linear carbon chains Kroto wanted to study were in fact being produced in abundance. In addition, they reported a bizarre pattern among the larger clusters: the distribution was strikingly lacking in the species having an odd number of atoms.

The Exxon researchers recorded but did not notice that two particular even-numbered members, C_{60} and C_{70}, were somewhat more abundant than their neighbors [*see bottom illustration on page 58*]. The mysterious even-numbered distribution of clusters was separated from the small linear-chain distribution by what appeared to be something of a forbidden zone—a region of clusters between roughly 25 and 35 atoms in size in which few if any clusters could be detected.

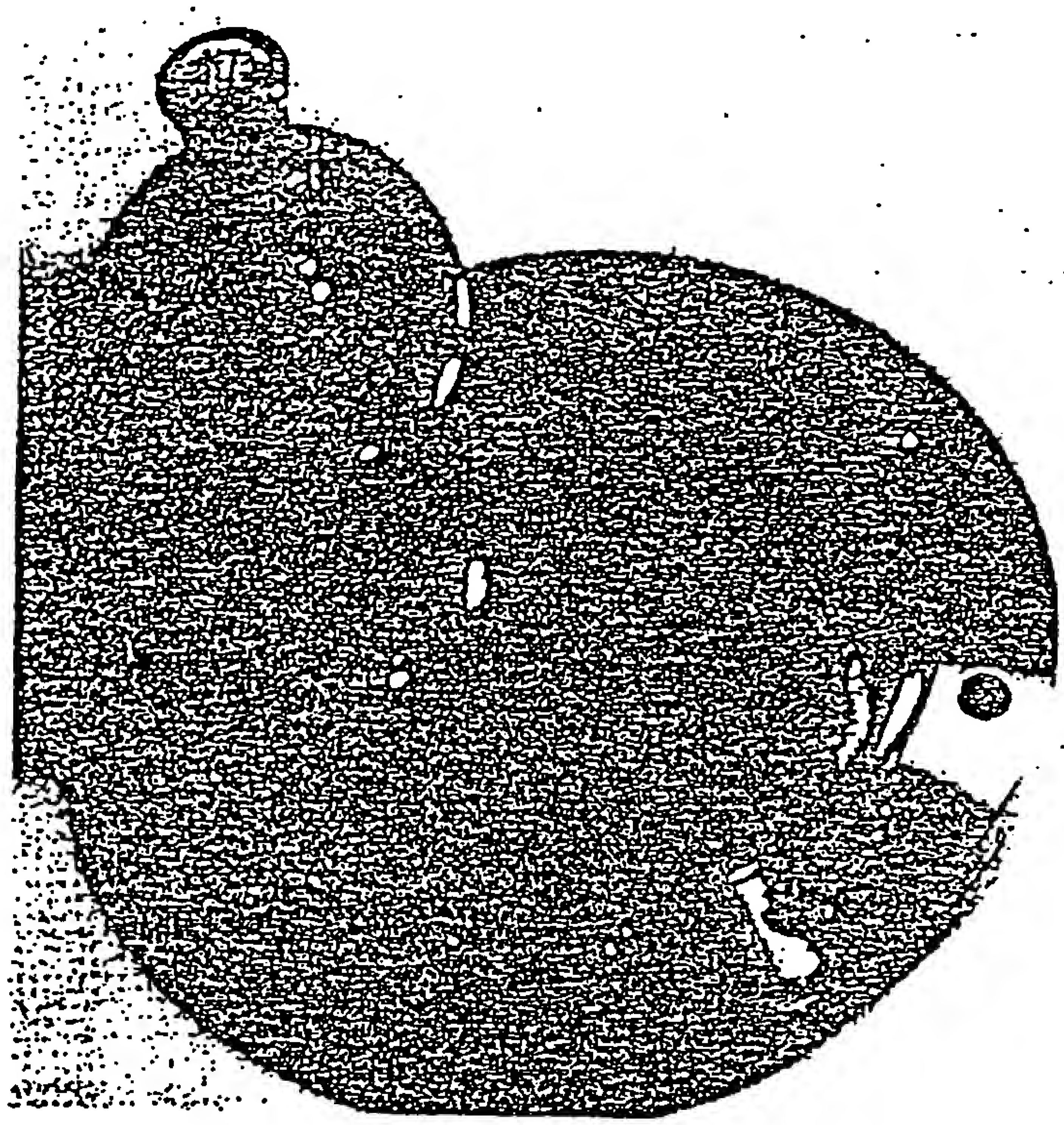
The even-numbered distribution was soon discovered to result from the fullerenes. In one of our many studies of Kroto's linear carbon chains, we reproduced the Exxon results but found something quite striking about the distribution of large, even-numbered clusters. Heath, Kroto and O'Brien noticed that the 60th cluster seemed five times more abundant than any other even-numbered cluster in the range between 50 and 70 atoms. This differential was dramatically greater than anything that had been seen before.

After much discussion, Heath and O'Brien spent the next weekend playing with the conditions in the laser-vaporization machine's supersonic nozzle. By Monday morning they had managed to find conditions in which C_{60} stood out in the cluster distribution like a flagpole. By the next morning we had had our Eureka! experience, and we were playing with every sort of soccerball we could get our hands on.

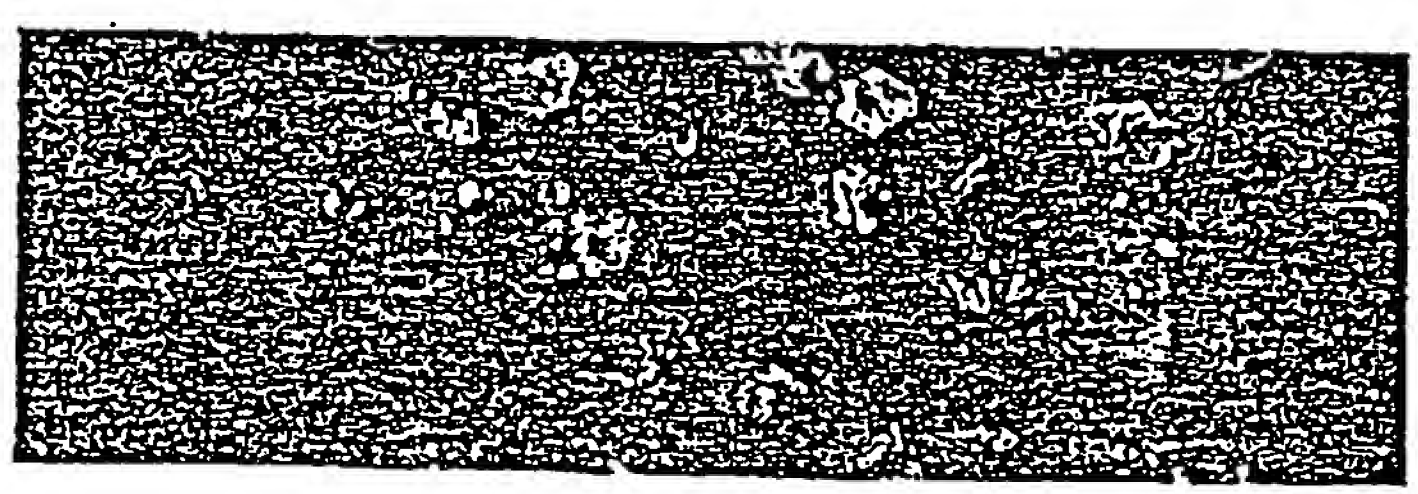
We found that we could explain the dominance of the even-numbered clusters by assuming they had all taken the structure of hollow, geodesic domes. They were all fullerenes. We could also argue that some fullerenes were more abundant than others because of the smoothness of the clusters' surface and the natural grouping of pentagons.

Pentagons provided an important clue. Although hundreds of examples are known in chemistry of five-membered rings attached to six-membered rings in stable aromatic compounds (for example, the nucleic acids adenine and guanine), only a few occur whose two five-membered rings share an edge. Interestingly, the smallest fullerene in which pentagons need not share an edge is C_{60}; the next is C_{70}. Although C_{72} and all larger fullerenes can easily adopt structures in which the five-membered rings are well separated, one finds that these pentagons in the larger fullerenes occupy strained positions. This vulnerability makes the carbon atoms at such sites particularly susceptible to chemical attack.

The big question, however, was not why fullerenes were stable but rather how they formed so readily in laser-vaporized graphite. Near the end of 1985, we suggested that the process began with linear chains. As the carbon vapor began to condense, the linear chains would grow long enough to flip back on themselves to form large monocyclic Hula-Hoops. As the growth continued, the chains would also fold into more effectively connected polycyclic network structures. Because graphite,



COLOR OF C_{60} depends on its form. This yellow film was sublimed onto a glass window that had been bolted to a vacuum oven. The benzene solution is magenta.



FULLERENE CRYSTALS were produced by evaporating a benzene solution of C_{60} containing a significant admixture of C_{70}.

the most stable known form of carbon, has its atoms bound in infinite hexagonal sheets, we suspected that the polycyclic network clusters resembled pieces of such sheets. We expected it to look like a fragment of chicken wire.

Like a cutout section of chicken wire, these graphitic sheets would have many dangling bonds, making them chemically reactive—much more so than the smaller linear chains, which have only two such bonds, one on each end. The sheets, therefore, would not be expected to be abundant in the cluster beams. Almost as soon as they form, they react with other small carbon molecules and grow too large to be seen. This, we believe, explains why there is a forbidden zone between the small linear-chain distribution and the first small fullerenes.

Chemists are conditioned to think of

Fullerene Electronics

Currently the most technologically interesting properties of bulk C_{60} are electronic: in various compound forms it functions as an insulator, a conductor, a semiconductor and a superconductor.

The material crystallizes when C_{60} molecules pack together like Ping-Pong balls in a face-centered cubic lattice. Calculations over the past few months have predicted that this new material is a direct band-gap semiconductor like gallium arsenide. All its units stand precisely at their posts in a crystalline structure. But unlike the elements of gallium arsenide, the buckyballs spin freely and at random. This disorder gives them a certain resemblance to amorphous silicon—a constituent of inexpensive solar cells. The peculiar disorder within order of bulk C_{60} has yet to be fully explored, but it is expected to produce a wholly new kind of semiconductor.

Early in 1991 researchers at AT&T Bell Laboratories discovered that they could mix, or dope, C_{60} with potassium to produce a new metallic phase—a "buckide" salt. It reaches its maximum electrical conductivity when there are three potassium atoms to each buckyball. If too much potassium is added, however, the material becomes insulating. Subsequent work has shown that K_3C_{60} is a stable metallic crystal consisting of a face-centered cubic structure of buckyballs, with potassium ions filling the cavities between the balls. Potassium buckide is the first completely three-dimensional molecular metal.

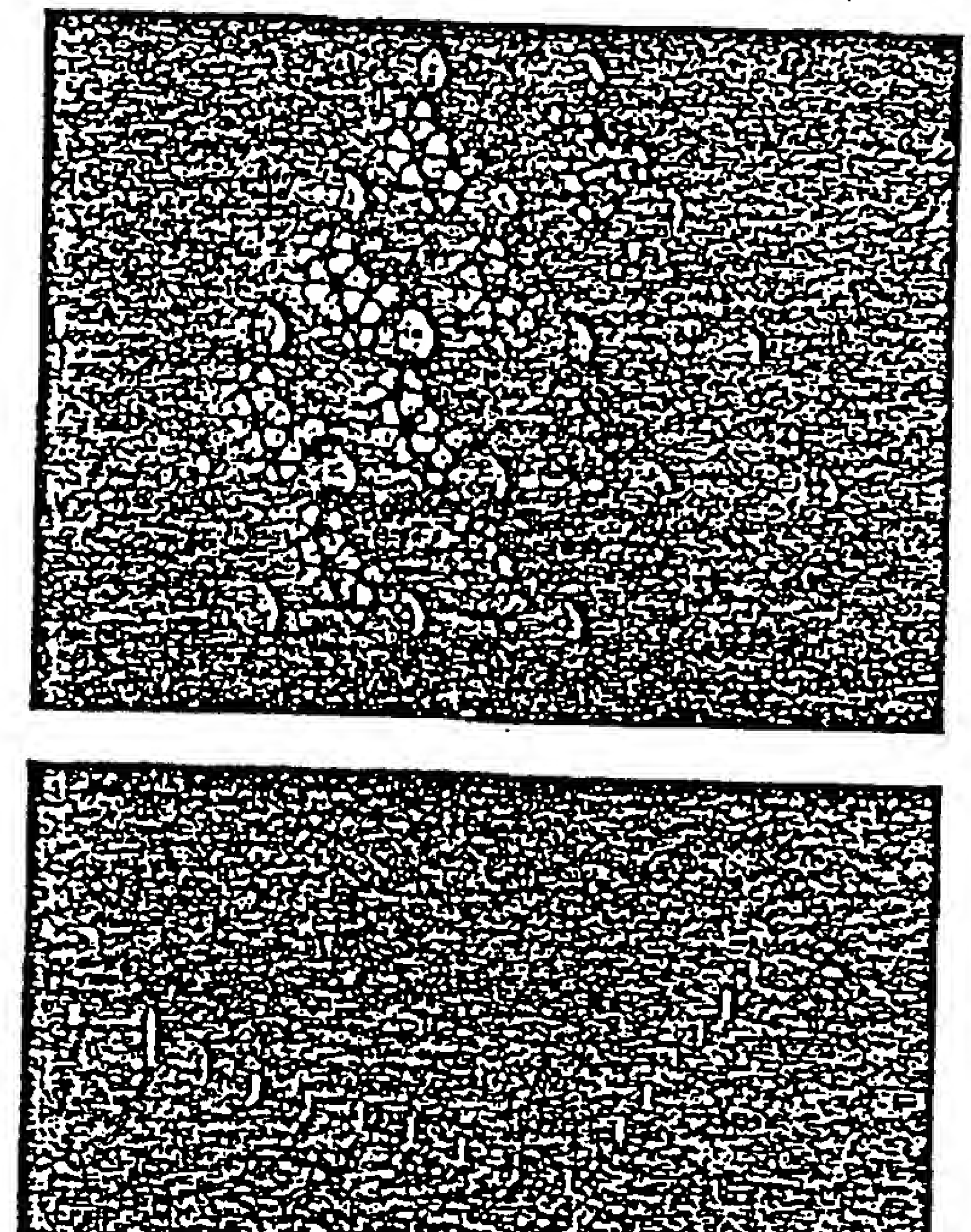
The Bell Labs team further discovered that this K_3C_{60} metal becomes a superconductor when cooled below 18 kelvins. When rubidium is substituted for the potassium, the critical temperature for superconductivity was found to be near 30 kelvins. (Recently workers at Allied-Signal, Inc., detected superconductivity at 43 kelvins for rubidium-thallium–doped material.) Careful work at the University of California at Los Angeles has shown that the superconducting phase is stable and readily annealed—imperfections can be smoothed away by heating and cooling.

The material can therefore be manufactured as a three-dimensional superconductor, making it a candidate for practical superconducting wires. Early estimates of magnetic and other characteristics indicate that these superconducting buckide salts are similar to the high-temperature superconducting ceramics made of yttrium, barium and copper oxide.

Recent work at the University of Minnesota has shown that highly ordered C_{60} films can readily be grown on crystalline substrates, such as gallium arsenide. This attribute makes the film a suitable material for microelectronic fabrication. Beautifully regular films of the K_3C_{60} superconductor can also be made [*see micrograph at right*], and the interface between the C_{60} crystalline film and the K_3C_{60} material has been found to be stable. It may thus lend itself to the production of intricately layered microelectronic devices.

In order for the semiconducting properties of fullerene materials to be thoroughly exploited, scientists need to learn how to dope them selectively to make *n*-type and *p*-type fullerene films, which donate electrons and holes, respectively. Such doping may involve putting a dopant atom inside the cage, either by growing the cage around the atom or by shooting atoms through the carbon walls by brute force. Small atoms, such as helium, have already been injected this way into the C_{60} cage, and it seems likely that hydrogen and lithium are insertable as well.

The versatility of bulk C_{60} seems to grow week by week. As we go to press, for example, there is a report suggesting that fullerene complexes exhibit ferromagnetic qualities in the absence of metals, an unparelleled phenomenon. Also, British workers from the universities of Leicester, Southampton and Sussex have just reported the generation of macroscopic quantities of fully fluorinated buckyballs ($C_{60}F_{60}$). The resulting "teflon balls" may be among the world's best lubricants. We do not know what the fullerenes' burgeoning traits will allow, but it would be surprising if the possibilities are not wonderful.

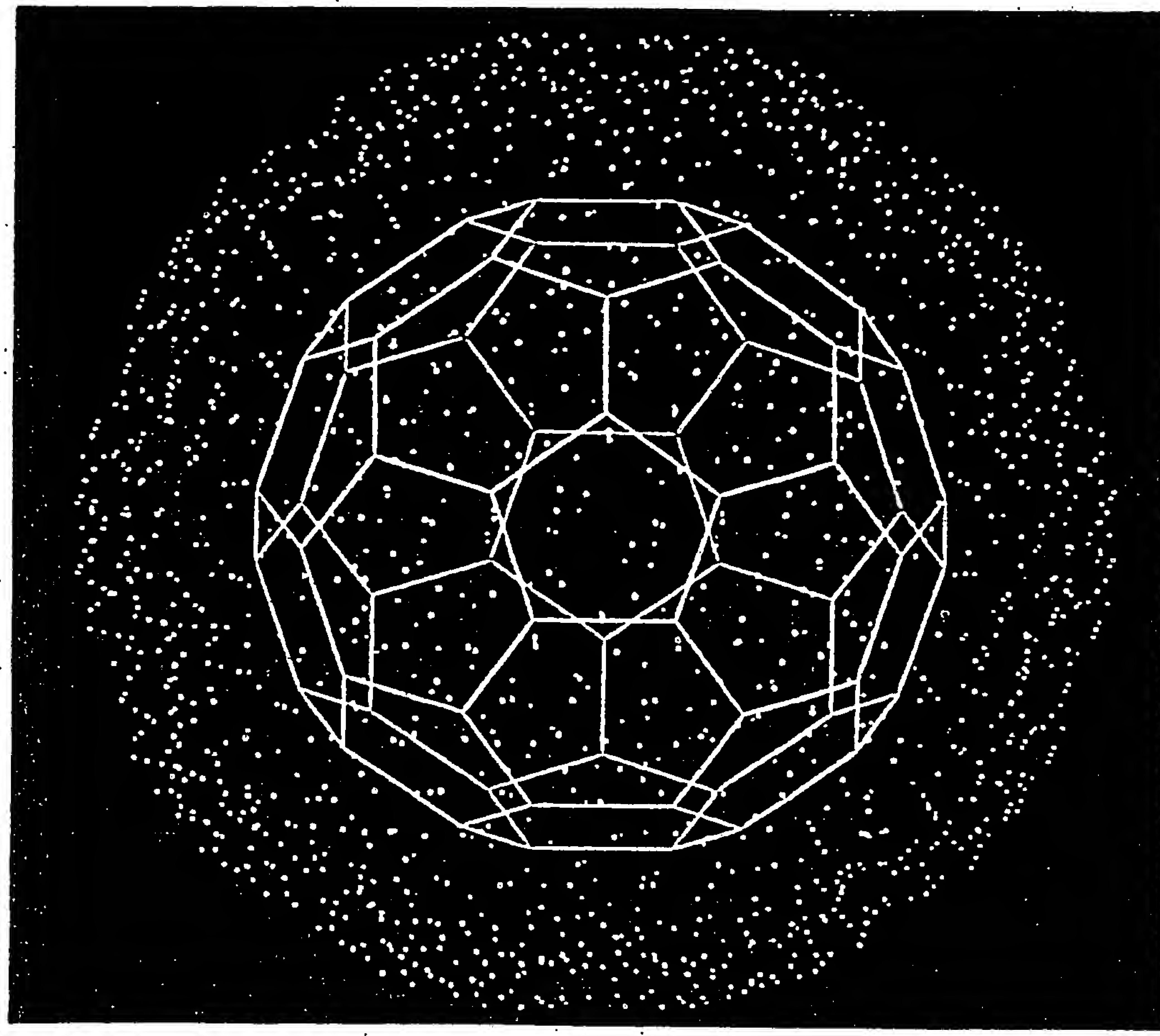


SUPERCONDUCTING FULLERIDE forms when buckyballs are doped with potassium in the ratio of K_3C_{60} (*diagram*), producing a crystal that can be grown on a gallium arsenide substrate (*scanning tunneling micrograph*).

nature

INTERNATIONAL WEEKLY JOURNAL OF SCIENCE

Volume 318 No 6042 14-20 November 1985 £1.90



SIXTY-CARBON CLUSTER

AUTUMN BOOKS

Harvey Brooks
(transformation of MIT)

P. N. Johnson-Laird
(brain and mind)

Anthony W. Clare
(psychoanalysis as religion)

A. O. Lucas
(war on disease)

Hendrik B. G. Casimir
(physics and physicists)

Gordon Thompson
(dimensions of nuclear proliferation)

Jacques Ninio
(origins of life)

Edward Harrison
(steps through the cosmos)

KROTO EXHIBIT 12

C_{60}: Buckminsterfullerene

H. W. Kroto*, J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley

Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.

During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells[1], graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. This object is commonly encountered as the football shown in Fig. 1. The C_{60} molecule which results when a carbon atom is placed at each vertex of this structure has all valences satisfied by two single bonds and one double bond, has many resonance structures, and appears to be aromatic.

The technique used to produce and detect this unusual molecule involves the vaporization of carbon species from the surface of a solid disk of graphite into a high-density helium flow, using a focused pulsed laser. The vaporization laser was the second harmonic of Q-switched Nd:YAG producing pulse energies of ~30 mJ. The resulting carbon clusters were expanded in a supersonic molecular beam, photoionized using an excimer laser, and detected by time-of-flight mass spectrometry. The vaporization chamber is shown in Fig. 2. In the experiment the pulsed valve was opened first and then the vaporization laser was fired after a precisely controlled delay. Carbon species were vaporized into the helium stream, cooled and partially equilibrated in the expansion, and travelled in the resulting molecular beam to the ionization region. The clusters were ionized by direct one-photon excitation with a carefully synchronized excimer laser pulse. The apparatus has been fully described previously[2-5].

The vaporization of carbon has been studied previously in a very similar apparatus[6]. In that work clusters of up to 190 carbon atoms were observed and it was noted that for clusters of more than 40 atoms, only those containing an even number of atoms were observed. In the mass spectra displayed in ref. 6, the C_{60} peak is the largest for cluster sizes of >40 atoms, but it is not completely dominant. We have recently re-examined this system and found that under certain clustering conditions the C_{60} peak can be made about 40 times larger than neighbouring clusters.

Figure 3 shows a series of cluster distributions resulting from variations in the vaporization conditions evolving from a cluster distribution similar to that observed in ref. 3, to one in which C_{60} is totally dominant. In Fig. 3c, where the firing of the vaporization laser was delayed until most of the He pulse had passed, a roughly gaussian distribution of large, even-numbered clusters with 38–120 atoms resulted. The C_{60} peak was largest but not dominant. In Fig. 3b, the vaporization laser was fired at the time of maximum helium density; the C_{60} peak grew into a feature perhaps five times stronger than its neighbours, with the exception of C_{70}. In Fig. 3a, the conditions were similar to those in Fig. 3b but in addition the integrating cup depicted in Fig. 2 was added to increase the time between vaporization and expansion. The resulting cluster distribution is completely dominated by C_{60}, in fact more than 50% of the total large cluster abundance is accounted for by C_{60}; the C_{70} peak has diminished in relative intensity compared with C_{60}, but remains rather prominent, accounting for ~5% of the large cluster population.

Our rationalization of these results is that in the laser vaporization, fragments are torn from the surface as pieces of the planar graphite fused six-membered ring structure. We believe that the distribution in Fig. 3c is fairly representative of the nascent distribution of larger ring fragments. When these hot ring clusters are left in contact with high-density helium, the clusters equilibrate by two- and three-body collisions towards the most stable species, which appears to be a unique cluster containing 60 atoms.

When one thinks in terms of the many fused-ring isomers with unsatisfied valences at the edges that would naturally arise from a graphite fragmentation, this result seems impossible: there is not much to choose between such isomers in terms of stability. If one tries to shift to a tetrahedral diamond structure, the entire surface of the cluster will be covered with unsatisfied valences. Thus a search was made for some other plausible structure which would satisfy all sp^2 valences. Only a spheroidal structure appears likely to satisfy this criterion, and thus Buckminster Fuller's studies were consulted (see, for example, ref. 7). An unusually beautiful (and probably unique) choice is the truncated icosahedron depicted in Fig. 1. As mentioned above, all valences are satisfied with this structure, and the molecule appears to be aromatic. The structure has the symmetry of the icosahedral group. The inner and outer surfaces are covered with a sea of π electrons. The diameter of this C_{60} molecule is ~7 Å, providing an inner cavity which appears to be capable of holding a variety of atoms[8].

Assuming that our somewhat speculative structure is correct, there are a number of important ramifications arising from the existence of such a species. Because of its stability when formed under the most violent conditions, it may be widely distributed in the Universe. For example, it may be a major constituent of circumstellar shells with high carbon content. It is a feasible constituent of interstellar dust and a possible major site for

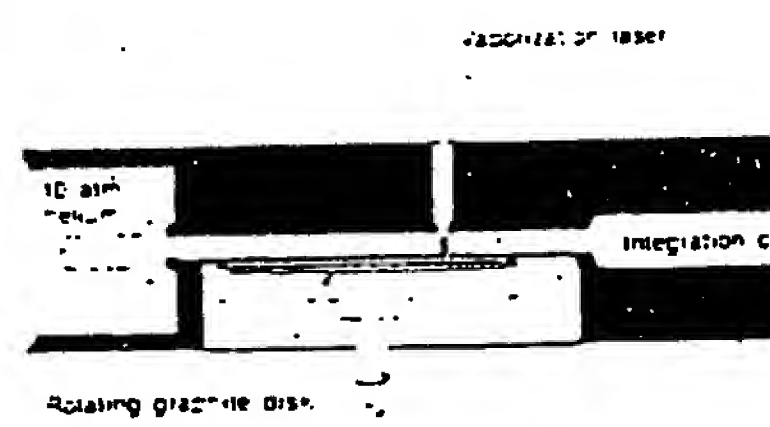


Fig. 2 Schematic diagram of the pulsed supersonic nozzle used to generate carbon cluster beams. The integrating cup can be removed at the indicated line. The vaporization laser beam (30–40 mJ at 532 nm in a 5-ns pulse) is focused through the nozzle, striking a graphite disk which is rotated slowly to produce a smooth vaporization surface. The pulsed nozzle passes high-density helium over this vaporization zone. This helium carrier gas provides the thermalizing collisions necessary to cool, react and cluster the species in the vaporized graphite plasma, and the wind necessary to carry the cluster products through the remainder of the nozzle. Free expansion of this cluster-laden gas at the end of the nozzle forms a supersonic beam which is probed 1.3 m downstream with a time-of-flight mass spectrometer.

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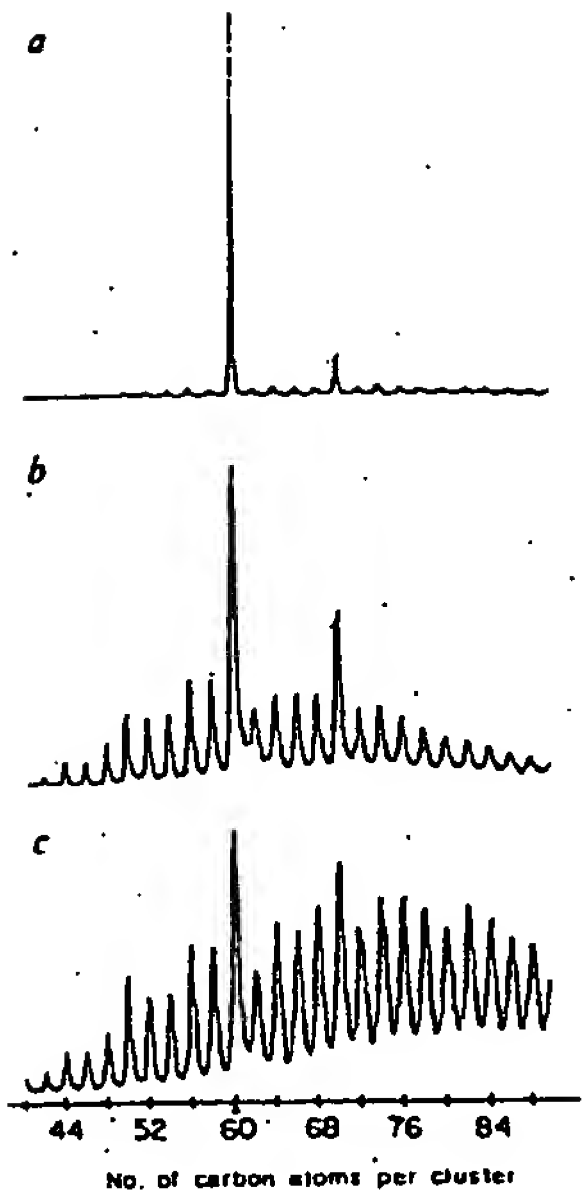

Fig. 3 Time-of-flight mass spectra of carbon clusters prepared by laser vaporization of graphite and cooled in a supersonic beam. Ionization was effected by direct one-photon excitation with an ArF excimer laser (6.4 eV, 1 mJ cm^{-2}). The three spectra shown differ in the extent of helium collisions occurring in the supersonic nozzle. In *c*, the effective helium density over the graphite target was less than 10 torr—the observed cluster distribution here is believed to be due simply to pieces of the graphite sheet ejected in the primary vaporization process. The spectrum in *b* was obtained when roughly 760 torr helium was present over the graphite target at the time of laser vaporization. The enhancement of C_{60} and C_{70} is believed to be due to gas-phase reactions at these higher clustering conditions. The spectrum in *a* was obtained by maximizing these cluster thermalization and cluster–cluster reactions in the 'integration cup' shown in Fig. 2. The concentration of cluster species in the especially stable C_{60} form is the prime experimental observation of this study.

surface-catalysed chemical processes which lead to the formation of interstellar molecules. Even more speculatively, C_{60} or a derivative might be the carrier of the diffuse interstellar lines[9].

If a large-scale synthetic route to this C_{60} species can be found, the chemical and practical value of the substance may prove extremely high. One can readily conceive of C_{60} derivatives of many kinds—such as C_{60} transition metal compounds, for example, $C_{60}Fe$ or halogenated species like $C_{60}F_{60}$ which might be a super-lubricant. We also have evidence that an atom (such as lanthanum[8] and oxygen[1]) can be placed in the interior, producing molecules which may exhibit unusual properties. For example, the chemical shift in the NMR of the central atom should be remarkable because of the ring currents. If stable in macroscopic, condensed phases, this C_{60} species would provide a topologically novel aromatic nucleus for new branches of organic and inorganic chemistry. Finally, this especially stable and symmetrical carbon structure provides a possible catalyst and/or intermediate to be considered in modelling prebiotic chemistry.

We are disturbed at the number of letters and syllables in the rather fanciful but highly appropriate name we have chosen in the title to refer to this C_{60} species. For such a unique and centrally important molecular structure, a more concise name would be useful. A number of alternatives come to mind (for example, ballene, spherene, soccerene, carbosoccer), but we prefer to let this issue of nomenclature be settled by consensus.

We thank Frank Tittel, Y. Liu and Q. Zhang for helpful discussions, encouragement and technical support. This research was supported by the Army Research Office and the Robert A. Welch Foundation, and used a laser and molecular beam apparatus supported by the NSF and the US Department of Energy. H.W.K. acknowledges travel support provided by SERC, UK. J.R.H. and S.C.O'B. are Robert A. Welch Predoctoral Fellows.

Received 13 September; accepted 18 October 1985.

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Printed in Great Britain by Macmillan Production Ltd., Basingstoke, Hampshire

The Nobel Prize in Chemistry 1996

"for their discovery of fullerenes"

Press release

The Fullerene Gallery

Robert F. Curl, Jr.

USA

Rice University
Houston, USA

1933 -

Autobiography

Sir Harold W. Kroto

U.K.

University of Sussex,
Brighton, U.K.

1939 -

Autobiography

Richard E. Smalley

USA

Rice University,
Houston, USA

1943 -

Autobiography

KROTO EXHIBIT 13

Press Release: The 1996 Nobel Prize in Chemistry

KUNGL. VETENSKAPSAKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

9 October 1996

The Royal Swedish Academy of Sciences has decided to award the 1996 Nobel Prize in Chemistry to

Professor **Robert F. Curl, Jr.**, Rice University, Houston, USA,
Professor **Sir Harold W. Kroto**, University of Sussex, Brighton, U.K., and
Professor **Richard E. Smalley**, Rice University, Houston, USA,

for their discovery of fullerenes.

Note: This document is made for Netscape 2.0 or later, and some of the chemical formulas might not appear as intended using other browsers.

The discovery of carbon atoms bound in the form of a ball is rewarded

New forms of the element carbon - called fullerenes - in which the atoms are arranged in closed shells was discovered in 1985 by **Robert F. Curl, Harold W. Kroto** and **Richard E. Smalley**. The number of carbon atoms in the shell can vary, and for this reason numerous new carbon structures have become known. Formerly, six crystalline forms of the element carbon were known, namely two kinds of graphite, two kinds of diamond, chaoit and carbon(VI). The latter two were discovered in 1968 and 1972.

Fullerenes are formed when vaporised carbon condenses in an atmosphere of inert gas. The gaseous carbon is obtained e.g. by directing an intense pulse of laser light at a carbon surface. The released carbon atoms are mixed with a stream of helium gas and combine to form clusters of some few up to hundreds of atoms. The gas is then led into a vacuum chamber where it expands and is cooled to some degrees above absolute zero. The carbon clusters can then be analysed with mass spectrometry.

Curl, Kroto and Smalley performed this experiment together with graduate students J.R. Heath and S.C. OBrien during a period of eleven days in 1985. By fine-tuning the experiment they were able in particular to produce clusters with 60 carbon atoms and clusters with 70. Clusters of 60 carbon atoms, C_{60}, were the most abundant. They found high stability in C_{60}, which suggested a molecular structure of great symmetry. It was suggested that C_{60} could be a "truncated icosahedron cage", a polyhedron with 20 hexagonal (6-angled) surfaces and 12 pentagonal (5-angled) surfaces. The pattern of a European football has exactly this structure, as does the geodetic dome designed by the American architect R. Buckminster Fuller for the 1967 Montreal World Exhibition. The researchers named the newly-discovered structure *buckminsterfullerene* after him.

The discovery of the unique structure of the C_{60} was published in the journal *Nature* and had a mixed reception - both criticism and enthusiastic acceptance. No physicist or chemist had expected that carbon would be found in such a symmetrical form other than those already known. Continuing their work during 1985-90, Curl, Kroto and Smalley obtained further evidence that the proposed structure ought to be correct. Among other things they succeeded in identifying carbon clusters that enclosed one or more metal atoms. In 1990 physicists W. Krätschmer and D.R. Huffman for the first time produced isolable quantities of C_{60} by causing an arc between two graphite rods to burn in a helium atmosphere and extracting the carbon condensate so formed using an organic solvent. They obtained a mixture of C_{60} and C_{70}, the structures of which could be determined. This confirmed the correctness of the C_{60} hypothesis. The way was thus open for studying the chemical properties of C_{60} and other carbon clusters such as C_{70}, C_{76}, C_{78} and C_{84}. New substances were produced from these compounds, with new and unexpected properties. An entirely new branch of chemistry developed, with consequences in such diverse areas as astrochemistry, superconductivity and materials chemistry/physics.

Background

Many widely diverse research areas coincide in the discovery of the fullerenes. **Harold W. Kroto** was at the time active in microwave spectroscopy, a science which thanks to the growth of radioastronomy can be used for analysing gas in space, both in stellar atmospheres and in interstellar gas clouds. Kroto was particularly interested in carbon-rich giant stars. He had discovered and investigated spectrum lines in their atmospheres and found that they could be ascribed to a kind of long-chained molecule of only carbon and nitrogen, termed cyanopolyynes. The same sort of molecules is also found in interstellar gas clouds. Kroto's idea was that these carbon compounds had been formed in stellar atmospheres, not in clouds. He now wished to study the formation of these long-chain molecules more closely.

He got in touch with **Richard E. Smalley**, whose research was in cluster chemistry, an important part of chemical physics. A cluster is an aggregate of atoms or molecules, something in between microscopic particles and macroscopic particles. Smalley had designed and built a special *laser-supersonic cluster beam apparatus* able to vaporise almost any known material into a plasma of atoms and study the design and distribution of the clusters. His paramount interest was clusters of metal atoms, e.g. metals included in semiconductors, and he often performed these investigations together with **Robert F. Curl**, whose background was in microwave and infra-red spectroscopy.

Atoms form clusters

When atoms in a gas phase condense to form clusters, a series is formed where the size of the clusters varies from a few atoms to many hundreds. There are normally two size maxima visible in the distribution curve, one around small clusters and one around large. It is often found that cer-tain cluster sizes may dominate, and the number of atoms in these is termed a "magic number", a term borrowed from nuclear physics. These dominant cluster sizes were assumed to have some special property such as high symmetry.

Fruitful contact

Through his acquaintanceship with Robert Curl, Kroto learned that it should be possible to use Smalley's instrument to study the vaporisation and cluster formation of carbon, which might afford him evidence that the long-carbon-chain compounds could have been formed in the hot parts of stellar atmospheres. Curl conveyed this interest to Smalley and the result was that on 1 September 1985 Kroto arrived in Smalley's laboratory to start, together with Curl and Smalley, the experiments on carbon vaporisation. In the course of the work it proved possible to influence drastically the size distribution of the carbon clusters where, predominantly, 60 appeared as a magic number but also 70 (Fig. 1). The research group

now got something else to think about. Instead of long carbon chains, the idea arose that the C_{60} cluster could have the structure of a truncated (cut off) icosahedron (Fig. 2) since its great stability was assumed to correspond to a closed shell with a highly symmetrical structure. C_{60} was given a fanciful name, buckminsterfullerene, after the American architect R. Buckminster Fuller, inventor of the geodesic dome. This hectic period ended on 12 September with the despatch of a manuscript entitled *C_{60}: Buckminsterfullerene* to *Nature*. The journal received it on 13 September and published the article on 14 November 1985.

Sensational news

For chemists the proposed structure was uniquely beautiful and satisfying. It corresponds to an aromatic, three-dimensional system in which single and double bonds alternated, and was thus of great theoretical significance. Here, moreover, was an entirely new example from a different research tradition with roots in organic chemistry: producing highly symmetrical molecules so as to study their properties. The Platonic bodies have often served as patterns, and hydrocarbons had already been synthesised as tetrahedral, cubic or dodecahedral (12-sided) structures.

Carbon atoms per cluster

Fig. 1
Using mass spectroscopy it was found that the size distribution of carbon clusters could be drastically affected by increasing the degree of chemical "boiling" in the inlet nozzle to the vacuum chamber. Clusters with 60 and 70 carbon atoms could be produced. (Acc. Chem. Res., Vol. 25, No. 3, 1992)

Fig. 2
Models of the structures of C_{60}. (Acc. Chem. Res., Vol. 25, No. 3, 1992)

Further investigations

To gain further clarity Curl, Kroto and Smalley continued their investigations of C_{60}. They attempted to make it react with other compounds. Gases such as hydrogen, nitrous oxide, carbon monoxide, sulphur dioxide, oxygen or ammonia were injected into the gas stream, but no effect on the C_{60} peak recorded in the mass spectrometer could be demonstrated. This showed that C_{60} was a slow-reacting compound. It also turned out that all carbon clusters with an even number of carbon atoms from 40-80 (the interval that could be studied) reacted equally slowly. Analogously with C_{60} all these should then correspond to entirely closed structures, resembling cages. This was in agreement with Euler's law, a mathematical proposition which states that for any polygon with *n* edges, where *n* is an even number greater than 22, at least one polyhedron can be constructed with 12 pentagons and $(n-20)/2$ hexagons, which, in simple terms, states that it is possible with 12 pentagons and with none or more than one hexagon to construct a polyhedron. For large *n* many different closed structures can occur, thus also for C_{60}, and it was presumably the beautiful symmetry of the proposed structure that gave it the preference.

The combination of chemical inertia in clusters with even numbers of carbon atoms and the possibility that all these could possess closed structures in accordance with Euler's law, led to the proposal that all these carbon clusters should have closed structures. They were given the name fullerenes and conceivably an almost infinite number of fullerenes could exist. The element carbon had thus assumed an almost infinite number of different structures.

C_{60} and metals

New experiments were rapidly devised to test the C_{60} hypothesis. Since the C_{60} structure is hollow, with room for one or more other atoms, attempts were made to enclose a metal atom. A graphite sheet was soaked with a solution of a metal salt (lanthanum chloride, $LaCl_3$) and subjected to vaporisation-condensation experiments. Masspectroscopic analysis of the clusters formed showed the presence of $C_{60}La^+$. These proved to be photoresistant, i.e. irradiation with intense laser light did not remove the metal atoms. This reinforced the idea that metal atoms were captured inside the cage structure.

The possibility of producing clusters with a metal atom enclosed gave rise to what was termed the "shrink-wrapping" experiment. Ions of one and the same size or at least similar sizes were gathered in a magnetic trap and subjected to a laser pulse. It then turned out that the laser beam caused the carbon cage to shrink by 2 carbon atoms at a time: at a certain cage size, when the pressure on the metal atom inside

became too great, the fragmentation ceased. The shell had then shrunk so that it fitted exactly around the metal atom. For $C_{60}Cs^+$ this size was at $C_{48}Cs^+$, for $C_{60}K^+$ it was at $C_{44}K^+$ and for C_{60}^+ at C_{32}^+.

Further strong evidence gave rise to new chemistry

At the end of the 1980s, strong evidence was available that the C_{60} hypothesis was correct. In 1990 the synthesis of macroscopic quantities of C_{60} through carbon arc vaporisation between two graphite electrodes permitted the attainment of full certainty - the whole battery of methods for structure determination could be applied to C_{60} and other fullerenes and completely confirmed the fullerene hypothesis. As opposed to the other forms of carbon the fullerenes represent well-defined chemical compounds with in some respects new properties. A whole new chemistry has developed to manipulate the fullerene structure, and the properties of fullerenes can be studied systematically. It is possible to produce superconducting salts of C_{60}, new three-dimensional polymers, new catalysts, new materials and electrical and optical properties, sensors, and so on. In addition, it has been possible to produce thin tubes with closed ends, nanotubes, arranged in the same way as fullerenes. From a theoretical viewpoint, the discovery of the fullerenes has influenced our conception of such widely separated scientific problems as the galactic carbon cycle and classical aromaticity, a keystone of theoretical chemistry. No practically useful applications have yet been produced, but this is not to be expected as early as six years after macroscopic quantities of fullerenes became available.

Further reading

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